Egyptian Journal of Archaeological and Restoration Studies (*EJARS*)
An international peer-reviewed journal published bi-annually
www.ejars.sohag-univ.edu.eg

Review article

THE EFFECT OF IRON RUST STAINS ON HISTORICAL PAPERS AND THEIR REMOVAL USING DIFFERENT CLEANING METHODS: A REVIEW

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Article info.
EJARS – Vol. 15 (1) – June 2025: 1-11

Article history:
Received: 25-3-2024
Accepted: 12-8-2024
Doi: 10.21608/ejars.2025.434895

Keywords:
Historical paper manuscript
Iron rust stains
Deterioration
Analytical techniques
Cleaning techniques

Abstract:
Iron rust stains are considered one of the most dangerous stains that affect the components of historical paperdocuments and manuscripts in museums, libraries, and archives. They lead to a decrease in the chemical and physical stability of historical papers. This study aims to provide a comprehensive overview to understand thenature, formation, causes, aspects, and mechanisms of deterioration of iron rust stains on historical paper manuscripts and documents. It will offer a detailed explanation of all traditional and advanced methods used to remove them, as well as analytical techniques to identify them. The results indicate that the formation of ironrust stains (oxides such as Fe_3O_4, Fe_2O_3) is caused by the oxidation of iron ions by atmospheric oxidants (O_2) in the presence of water. There are various aspects of deterioration caused by iron rust stains, such as discoloration, holes, etc. Cleaning iron rust stains is a vital process in the treatment of paper manuscripts, as it helps prevent damage and increase the chemical stability of the manuscripts. There are many cleaning methods used to remove iron rust stains, each with its advantages and disadvantages. Restorers always opt forthe least damaging and most efficient method, such as mechanical cleaning, laser cleaning, plasma cleaning, etc. Various analytical methods are used to identify iron rust stains and explain their deterioration mechanism,such as X-ray analysis, microscopes, etc.

1. Introduction

Clips or staples are often used to fix or bind paper-based archives, documents, and books. Typically, these clips or staples are made of iron, making the papers susceptible to rusting, especially in high humidity conditions, fig. (1). Iron rust not only damages the papers but also causes them to become weak and brittle [1]. Rust is the result of a chemical reaction between iron and its surrounding environment. Iron forms various corrosion products, and the compoundsformed depend on the elements present at the time. Iron rust is mainly composed of iron oxides, chlorides, hydroxides, sulphides, and sulphates. The oxidation of iron ions byatmospheric oxidizers (O_2) under a layer of water (electrolyte) results in the formation of ironrust layers, which consist of oxides such as Fe_2O_3, Fe_3O_4, and hydroxides such as α-FeO (OH), β-FeO (OH), and γ-FeO (OH) [1-3]. Iron has a relatively strong negative electrode potential, causing the surface to corrode quickly. These layers are usually stable at a relative humidity (RH) of 50-60% or less and room temperature, and the risk of iron migration has significantly reduced but not completely stopped. However, when the relative humidity exceeds 60%, a layer of active corrosion, which is bright orange, friable, and considered active, quickly forms and migrates around the iron rust or ink line [1,4]. Iron corrosion is affecting the paper objects [2, 5]. In the early stages, the discoloration will only be visible on the metal objects themselves. An iron paperclip will turn brown because of rust. Later, the paper object will also become visibly discolored. In this case, the degradation to the object isslight. If there is significant discoloration on the object near the metal clips or staples, and ifthe degradation will be exacerbated by rough handling, the degradation is moderate. In a fewcases, holes can be seen in the discolored areas. If text is involved, the degradation is regardedas serious. An efficient cleaning technique for removing iron rust is important for the preservation of historical artifacts. The mechanism and rate of dissolution of iron oxides, which are the major component of iron rust, have been previously studied. There are severalissues related to cleaning, such as when to start cleaning and when to stop. An essential objective of all conservation procedures is to improve the stability of the chemical composition of the papers being treated. When carrying out cleaning in conservation works, the general features of iron rust and some of the factors that need to be considered are important [2,6]. Some authors discussed the presence of rust stains and an increase in pH. However, at the time of measurement, papers did not show the same neutralizing effect. A very similar outcome was observed for papers from the interior, an area rich in iron (III) compounds, indicating that iron rust is responsible for a decrease in pH compared to poor areas. The rusty spots in the papers that are rich in iron (rust stains) are the most acidic and more deteriorated. The presence of iron III (rust stains) in the papers catalyzes the breakdownof cellulose chains due to acid hydrolysis [2,7]. The dark brown iron rust, $Fe_2O_3.H_2O$ (or FeOOH), is difficult to remove because the stain is insoluble in both organic solvents and water. The cleaning method should be changed to remove the stain, which might have penetrated deeply into the papers. An effective method for removing iron rust from papers is reducing insoluble iron (III) oxide compounds into soluble iron (II) oxide compounds by using reducing agents [8,9]. Burgess [10] identifies cleaning as the removal of degradation products and rust removal from a surface object. Chemical solution techniques often use solutions of hydrogen peroxide, oxalic acid, potassium permanganate, etc. for cleaning. However, chemical agents remaining on the paper surface after treatment can accelerate theaging process of paper, leading to secondary damage. Therefore, it is important to consider alternatives to these acids for treatment, along with the use of a corrosion inhibitor. Some authors [9,11] reported using reducing agents to reduce insoluble ferric oxide compounds to soluble ferrous oxide compounds. Therefore, the application of a chelating agent is exploredas a potential solution to the issue of eliminating undesired stains and spots from paper artifacts. Chelating agents are organic compounds that complex metal ions, preventing themfrom participating in chemical reactions. Using chelating agents to remove iron stains [2,9]. Different solutions were used for the removal of iron rust, and a reducing agent (sodium dithionite) in combination with a chelating agent [ethylenediaminetetraacetic acid (EDTA)] was determined to be the best of the solutions tested [12, 13]. Furthermore, the use of severalchelating compounds as an alternative to EDTA was examined, and the synergistic process of removing iron rust by combining a reducing agent with a chelating agent was estimated [2]. Casaletto [13] explained that one of the disadvantages of chemical cleaning is that it cancause fibers to be detached or cause severe swelling in the papers. After the acid cleaning, athorough washing and rinsing procedure is necessary to remove any traces of acid or salts that may result from a chemical reaction during the cleaning. Abdel-Maksoud et al. [14] explained that radiation is a method used to physically remove deposits, including laser ablation, ultrasonic generators, and plasma. Abdel-Maksoud et al. [15] explained that laser-based techniques are often utilized as advanced cleaning techniques for artifact surfaces, avoiding or reducing both chemical and mechanical disruption of historical artifacts, and having the ability to remove contaminated dirt and coatings in particular conditions. Initially,laser beams were used for cleaning paintings and stones, but subsequently, several types of artworks have been cleaned, including metals, bones, wood, fossils, papers, and leather, etc.Plasma cleaning affects the surface of materials without altering the complex material properties. The plasma forms at near-ambient temperature, minimizing the degradation hazards to the heat-sensitive materials. Depending on conditions and process gases, plasma cleaning can modify surfaces. Plasma cleaning can be applied to various materials as well as complex surfaces. The processes that result in a selective, constrained alteration of the surface roughness (on a nanometric scale) are the main applications of plasma. For conservation and restoration of various historical objects, plasma cleaning is recommended in the cultural materials protection due to atmospheric conditions and low pressure. This review focuses on the impact of iron rust stains on paper artifacts, the main aspects of the resulting damage, and its deterioration mechanism, along with an explanation of the different cleaning methods.

Figure (1) the documents are contaminated with iron rust [1]

2. Degradation mechanisms

Each distinctive rust color on paper results from air pollution, low or high oxygen environments, and low or high moisture contents over time. The primary cause of yellow rustis an environment with high moisture content over time. Brown rust is crusty and dry and occurs when oxygen and water come into contact with localized patches on component surfaces. Black rust is the most stable form, occurring in a low-oxygen environment with lowmoisture. The rust residue appears where the reaction began, particularly in contact with chlorides [16]. Red rust occurs due to atmospheric causative factors, which are similar to those of black rust in an environment that contains chlorides. The primary cause of rust is thereaction between oxygen and iron in the presence of moisture. This reaction, known as oxidation, causes iron atoms to lose electrons, forming iron oxide (rust) [17]. In the presenceof oxygen and water, the Fe in the clips or staples is ionized and dissolved into Fe^{2+}, then hydrolyzed to $Fe(OH)^+$ and oxidized to become Fe. Rust is subsequently formed on the surface by the combination of Fe^{3+} and other elements [16, 18]. Oxygen molecules in water act as excellent oxidizing agents, undergoing reduction reactions, whereas the iron from steel,which is a reducing agent, gets oxidized at the anode. As a result, the following is the anodicreaction of the oxidation of Fe in the electrochemical cell when the iron atom releases electrons. Iron gall ink contains a significant amount of iron ions. Iron ions interact with peroxides formed during the oxidation of organic materials, thereby releasing highly interactivehydroxyl radicals. The reduction of iron (III) by many organic compounds, such as superoxide anions, enables these reactions to proceed in a repeating cycle. This cyclic process leads to considerable oxidative damage [19]. Because of the reducing agents present in the paper, notall of the Fe^{2+} is oxidized to Fe^{3+}. As a result, even hundreds of years after being written on paper, old iron gall inks can still have significant quantities of iron (II) ions [20]. Iron (II) ions are able to speed up the oxidative deterioration of cellulose through two mechanisms:

- Organic radicals are produced directly and then oxidized afterwards.

$$Fe^{2+}O_2 \rightarrow Fe^{3+}O_2 \bullet^- \text{ [5]}$$
$$Fe^{3+}O_2 \bullet^- + RH \rightarrow Fe^{2+} + HOO \bullet + R \bullet \text{ [16]}$$
$$R \bullet + O_2 \rightarrow ROO \text{ [16]}$$
$$ROO \bullet + R'H \rightarrow ROOH + R' \bullet \text{ [17]}$$

- The process involves the formation of hydrogen peroxide, which is then brokendown by iron (II) ions to produce a hydroxide ion and a hydroxyl radical.

$$Fe^{2+}ROO \bullet + H^+ \rightarrow Fe^{3+} + H_2O_2 \text{ [16]}$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^- \text{ [5]}$$
$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^- \text{ [17]}$$

Hydroxyl radicals are very reactive and mobile, especially in the presence of water to form hydrogen bonds, as is true hydrophilic materials such as paper. They easily take hydrogen from cellulose, thereby forming organic radicals. Hydroxyl radicals are often thought to be the main reactants to cellulose oxidative damage due to theirreactivity [16]. Taken hydrogen from the carbon atoms of the β-glycosidic bond betweenthe glucose units of the cellulose chain leads to the breakdown of these bonds, causing a reduction in the degree of polymerization and loss of mechanical strengthof the paper [16,20].

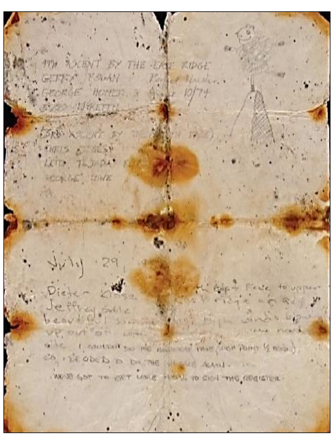

Figure (2) severe corrosion penetrated the paper from the metal box that stored the paper [8].

3. The Effect of Iron Rust on Papers

Iron metal is one of the primary reasons for tarnishing. This is due to the oxidative compounds present in papers, such as iron inks. The deterioration of paper artifacts can be seen through the corrosion of metal used in bookbinding or fixing paper-based materials. The deterioration of papers around clips results from severe corrosion of the metal when fire treatments or preservatives are used, in addition to the presence of H_2O and O_2 in paper [21]. These deteriorations can be ascribed to the original physical preservation conditions ofthe manuscript or to writers using different amounts of ink, which resulted in varying thicknesses or intensities as well as faded characters. Moreover, some documents have moreelements like decorations, diacritical marks, or writing in multiple colors made with iron or copper. Rust is a type of corrosion that happens when iron is exposed to moisture and oxygen [22,23]. It is a major issue in the cultural heritage, causing significant damage to structures and reducing their mechanical and chemical stability. Rust can decrease the strength, durability, and performance of papers. For instance, rust can weaken the structure of paper and make it crack or fall apart. It can also reduce the efficiency of mechanical properties, leading to increased weakness and brittleness. Rust can also affect the appearance of papers, making them unappealing and unsightly. Papers that have been discolored by rust are characterized by stains or areas that have an orange to brownish hue, which alters the paper's appearance, figs. (2 & 3). Since the discoloration is unsightly, paper conservators and conservationscientists have spent decades trying to remove rust stains from paper objects using a variety of cleaning methods. Wet paper artifacts not only cause iron ink or clips to corrode, but specific conditions are established when ink or clips are present in wet papers, which can accelerate the iron corrosion [24]. Strength declines as a result of the rusting of the metals and the degradation of the papers. The areas of the paper around the clips or staples are recurrently rusted and deteriorated due to the acids that accumulate in the paper fibers. The presence of rust stains causes an increase in pH, which was observed after two days. However, at the time of measurement, the papers did not show the same neutralizing effect.A very similar outcome was observed for papers from the interior, an area rich in iron (III) compounds, indicating that iron (rust) is responsible for a decrease in pH compared to poor areas. The rusty stains in the papers that are rich in iron (rust stains) are the most acidic and more deteriorated. Poggi et al. [25] discussed that the presence of iron III (rust stains) in thepapers catalyzes the breakdown of cellulose chains due to acid hydrolysis. Another long-termexperiment similarly confirmed the changes in oxidation indexes towards their initial value. The pH value changed concurrently, following the same pattern. There is a role of acids foundin the papers, which interact with iron compounds, and this is the reason for the observed differences in cellulose deterioration between rust stain spots compared to non-stained areas.The differences between rust stain spots and non-stained areas were analyzed for acid and the pH of the papers. The acids observed in the papers result from rust stains, as described previously, or via oxidative degradation reactions of the papers when the water content of thepapers was gradually reduced.

Figure (3) rust from metal paper clips on the left and metal staples on the right [26].

4. Cleaning Methods

Conservation of cultural heritage materials such as paper manuscripts, books, and documentsis the main focus of library conservation departments. Zekou et al. [27] explained that paperscan become contaminated or deteriorated due to aging or storage in poor conditions, leadingto issues such as stains, foxing, and the growth of fungi or bacteria. Conservators and scientists should characterize the origin of degradation in detail and then choose the most effective cleaning procedure. The evaluation of the preservation stage in chemical and biological terms is referred to as "direct prevention." The cleaning procedure must guaranteethat intrusive techniques are used only for the contaminated area and not for the brittle organic substrate of the papers [28] There are numerous advantages and disadvantages to allcleaning techniques. Coladonato et al. [29] reported that various cleaning methods are available based on the chemical, physical, and structural characteristics of the materials to be removed. Thus, the choice of a cleaning procedure for iron rust is dependent upon the size and condition of the paper artifact, as well as the nature and thickness of the iron rust. Cleaning corrosive layers is important because it can remove contaminants and make the form of the paper object being restored as well as its aspect visible. Paper objects can be cleaned using a variety of techniques, including chemical, mechanical, and electrochemical methods [29].

4.1. *Mechanical cleaning*

Mechanical cleaning is the term used when corrosion or dirt is physically removed from papers using an external force. Mechanical cleaning primarily involves using basic tools, and there is no requirement to use a machine. The main issue with mechanical cleaning is abrasion, as hard particles from rust stains can scratch soft surfaces when in motion. Particles are frequently sharp, which can cause paper fibers to be cut. Thus, one defect of mechanical cleaning is that it may include vibrating or blowing, which could cause detachment or separation of parts or even lead to serious damage to paper fibers, and may also cause abrasion of the papers. Additionally, foreign materials can penetrate into thepaper fibers and cause media degradation [30]. Mechanical cleaning involves the removal of superficial particulate matter or rust using small tools such as brushes, dental tools, erasers, and scalpels to complete the treatments. This depends on how hard and thick the corrosion layers are and on the durability of the papers. It is a cleaning technique that can be used on its own before a more involved intervention, such as aqueous deacidification. Mechanical cleaning should come before aqueous treatments, as corrosion may have penetrated into thepaper fibers and become fixed if the aqueous treatment is not performed before its removal [9].

4.2. *Chemical cleaning*

For paper conservation treatments, rust stains in papers pose a challenging issue. The rust ona paper artifact can vary in size, from completely covering it to just leaving behind a stain from rusted paper clips or staples. Rust, $Fe_2O_3.H_2O$ (or Fe OOH), is difficult to remove because it doesn't dissolve in water or organic solvents. The traditional method for removing rust from paper involves reducing the insoluble iron compounds to soluble ones [1,2,7]. For a variety of reasons, iron rust on papers has long been a hard issue for conservators. Iron in a ferric state is known as rust, or iron oxide (Iron III). Iron (III) does not dissolve in water and is not removable using pure water or solvents [12]. As a result, a two-step procedure is required for the most effective rust removal from paper. The first step involves using a reducing agent to reduce the ferric iron to its ferrous state. In a ferrous state, it readily dissolves in water and can be removed from paper [31]. It is necessary to remove the ferric iron after it has been reduced to ferrous iron. Often, a straightforward washing will suffice toremove the iron (II). In order to extract the soluble iron (II), laundry detergents use high amounts of water. However, paper treatments are often carried out in trays filled with still water. Iron (II) residue can be removed from water using a high-volume wash that uses a lotof water, but this method is slow and leaves a chance that iron (II) residue will remain in thewater. Due to the possibility of Iron (II) leftover in the water oxidizing back into Iron (III) and perhaps creating a new stain, an alternate technique for eliminating the soluble Iron (II)is required [31,32]. Chelating agents are organic substances that sequester or complex metal ions. The complex prevents the metal ions from participating in chemical reactions in whichthey would typically be able to. Chelating agents are utilized in paper conservation for two main purposes: they remove iron stains and stabilize bleach solutions, specifically hydrogenperoxide [33]. A chelating agent is a molecule that has two suitable functional groups, each with a donor atom that can combine with a metal atom by donating two electrons. In essence,the negatively charged center of the chelating molecule combines with a positively charged metal center. Chelating agents can be divided into two groups [10]: ***)** Complexes with the positively charged metal center. The pH affects both the proton loss and an acid's capacity to function as a powerful chelating agent. ***)** Basic compounds: which can donate electrons to a positive metal center, are characteristic of basic substances. The negative charge comes from a set of available electrons and doesnot require the loss of a proton or the presence of a negative charge. Chemical solution techniques commonly involve using solutions like potassium permanganate, hydrogen peroxide, and oxalic acid for cleaning. However, these chemical agents can leave residues on the paper surface that may speed up the aging process and cause secondary damage. Therefore, it is important to explore alternatives to traditional acidic treatments and consider using a corrosion inhibitor. [34,35]. Iron rust can only be removedusing chemical cleaning due to the nature of the discoloration and the risk of degrading the paper. Applying various ligands and reducing agents to the paper surface in the form of a poultice is the current method for removing rust. One chelating agent can have two acidic groups. Oxalic acid (HOOC-COOH) is an example of such a type of chelating agent. Ethylenediamine ($H_2N \bullet CH_2 - CH_2 \bullet NH_2$) is an example of a chelating agent with one acidicand two basic groups. One basic group can be present in the same chelating agent. One example of this type is glycine (H_2N-CH_2-COOH) [33]. These functional groups must besituated so that they allow a ring to form with a metal center acting as the closing member [33]. This is the second prerequisite for chelation to occur. Chelating agents are able to form complexes with metal centers in several locations. Studies have shown that EDTA catalyzes ink corrosion. These results can only be rationalized by the hypothesis that a substantial amount of ink corrosion results from iron (II)-catalyzed oxidation. Lignin acts as an antioxidant, inhibiting cellulose oxidation by chelating hydroxyl radicals and forming relatively stable radicals [16]. Colbourne [36] explained that diethylenetriaminepentaacetic acid (DTPA) effectively complexes with iron (II), while iron (III) salts remain unaffected. EDTA has a slightly lower formation constant than the iron (II) soluble product, but it is the most commonly used chelate in paper conservation. EDTA enhances iron (III) ions solubility in water through complex formation. Though EDTA also complexes iron (II) ions, this does not inhibit the Fenton reaction since the octahedral Fe (II)-EDTA complex retains the capacity to coordinate hydrogen peroxide [16]. Pemberton & Melzer (12) proposed that washing in a solution of 0.1 M EDTA and 5% w/v Triammonium citrate (TAC) effectively decreased iron ion concentrations. However, they have not provided detailed data to support this claim. Niehus et al. [11] reported that pretreatment with [diethylenetriamine-pentaacetic acid (DTPA)] can remove 30% of iron ions from historical papers, leaving most of the iron impurities in the cellulose matrix. Thiourea dioxide ($CH_4N_2O_2S$), an agent that is easily accessible, stable and has strong reducibility, was used to remove iron rust from paper objects [2]. Since sodium hydrosulfite is a reducing agent, although the impact is not stable, it helps the removal of stains in a minimum concentration in a short time. Iron stain may resurface and the reduced ferrous iron may re-oxidize. The reduced iron ions in paper can therefore be effectively removed by using a chelating agent EDTA together with [sodium dithionite ($Na_2S_2O_4$) (SDT)]. The complexing of metal ions will be easier and more thorough with increasing the EDTA concentration. A concentration of 3.0% is able to be accepted as sufficient for removing iron rust in a short period at pH 4.6 [33]. The addition of NaOH or KOH to the EDTA solution makes it alkaline, which lengthensthe stain removal process while improving its efficacy. Because of its acidic nature, EDTA treatment alone, while effective in removing iron stains, is not recommended for this use. To preserve the treated material's physical strength, it is best to utilize it together with alkalis [37-39]. Selwyn et al. [40] found that immersing the paper in a solution of 10% w/v sodium dithionite and 1% w/v Na_4 EDTA effectively reduced the iron ion concentration. The orange stain on the paper disappeared upon visual observation after washing it in the solution. The most efficient method tested for removing iron rust from papers in a reasonableamount of time was SDT combined with EDTA at a minimum concentration of 2%. According to the results, thiourea dioxide "TDO" proved to be a secure and effective reducing agent for iron rust removal from papers. The TDO concentration was higher, and the removal rate was rapid within 30 minutes [1]. However, the increased concentration requires a higher temperature to dissolve it, which degrades paper. Low temperature reduces the removal's effectiveness and precipitates TDO. [41]. However, with a 2.5% TDO solution low concentration, the rust could not be completely removed. Consequently, the ideal TDO concentration solution was 5% at 40°C. EDTA and TDO combined significantly improved the removal procedure [1]. Furthermore, there was a slight reduction in the tensile strength of the EDTA+TDO-treated paper, indicating extreme caution when treating brittle paper with this solution [1]. Furthermore, the study examined the use of several chelating compounds asan alternative to EDTA, and estimated the synergistic process of removing iron rust by combining a reducing agent with a chelating agent [2]. Wang et al. [42] found that phytic acid (PA) can effectively remove iron ions from papers, indicating that the reagent extracts iron ions from the documents. Recently, the most commonly referenced reducing agent for iron removal in the literature is sodium dithionite ($Na_2S_2O_4$). Although sodium dithionite has been shown to be successful in removing rust, there can be serious practical issues. Furthermore, its use typically requires treating objects in a fume hood, which can be problematic for large objects that do not fit in the hood [8].

$$1 - \underset{\textit{(Sodium dithionite)}}{Na_2S_2O_4} + 3H_2O \rightarrow \underset{\textit{(Sodium bisulfate)}}{NaHSO_4} + \underset{\textit{(Sodium bisulfite)}}{NaHSO_3} + 4H^+$$

$$2 - NaHSO_3 + Fe^{3+} \rightarrow NaHSO_4 + Fe^{2+}$$

Conversely, sodium metabisulfite ($Na_2S_2O_5$), a reducing agent, is not categorized as a hazardous material and contains one extra oxygen atom compared to sodium dithionate. Sodium metabisulfite combined with EDTA has been shown to significantly remove rustfrom paper, fig. (4) [8].

$$1 - \underset{\textit{(Sodium metabisulfite)}}{Na_2S_2O_5} + H_2O \rightarrow \underset{\textit{(Sodium bisulfite)}}{2NaHSO_3}$$

$$2 - 2NaHSO_3 \rightarrow 2S_2 + H_2O + 2Na^+$$

$$3 - SO_2 + H_2O \rightarrow H_2SO_3 \rightarrow HSO_3^- + H^+$$

$$4 - 2NaHSO_3 + Fe_2O_3 + 2H^+ \rightarrow 2NaHSO_4 + H_2O + 2Fe^{2+}$$

Naturally, sodium dithionite proved to be the more efficient chemical for removing rust deposits, but cost and safety have been shown to be significant obstacles to its use. Sodium metabisulfite was considerably safer and easier to obtain, but required much more time to treat and was only efficient on light-to-medium rust deposits [8,39]. Colbourne [36] suggested that sodium metabisulfite can be used as an alternative to SDT to minimize safety risks. Additionally, SDT is commonly combined with iron chelation therapy because sodium metabisulfite is not as effective.

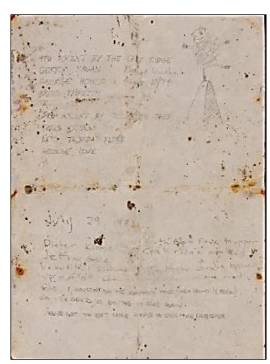

Figure (4) the paper after treatment with solutions containing 10% sodium metabisulfite combined with EDTA [8].

4.3. *Laser cleaning*

Recently, laser cleaning techniques have been extensively utilized in the field of cultural heritage cleaning. Conservators and scientists have spent decades studying the laser cleaning mechanism. However, it is still quite difficult to predict the final cleaning result. The physical procedures of laser cleaning are especially intricate, involving more than just the interactions between light and matter that transfer energy to the object surface, but also the conduction ofheat, subsequent dynamics of material, and phase shifts in the specimen material. Many variables affect these processes, including the laser parameters (laser speed, laser frequency,laser power, pulse width, etc.) and the degree of iron rusting. Laser cleaning is more difficultdue to the uncertainty of rust and variations in laser parameters. The cleaning mechanism in lasers is highly nonlinear and complex, making it impossible to describe with an equation [44,45]. The application of lasers in cultural heritage preservation has been enabled by the advancement of high-repetition-rate and high-power lasers, which are effective for cleaning and treating surfaces. Using lasers offers numerous advantages over traditional mechanical or chemical methods. It provides a dry procedure that reduces waste volume and can be automated [46]. Parfenov et al. [44] also stated that: **1)** Historical books and papers can be safely and efficiently cleaned by using a pulsed infrared laser with a wavelength of approximately 1 µm, fig. (5). **2)** High safety for cleaning paper is achieved by combining high-speed laser beam scanning with multi-pulse micromachining. Paper laser cleaning works best with the following parameters: average power of approximately 4 W (power density of about 2×105 W/cm^2), pulse repetition rate of about 20 kHz, scanning speed of 200 mm/s–500 mm/s, and pulse duration of around 10 ns. **3)** Excluding laser radiation from text and illustrations is important to protect documents and books from degradation during laser cleaning. Graphic and typographic text data from the laser processing area can be displayed by utilizing a high-precision laser beam scanning system. Some author successfully removed mold and foxing from old paper artifacts using a QS Nd:YAG laser operating at the second harmonic (532 nm) with fiber coupling. The process showed high selectivity and precise control, particularly when treating paper contaminated with metal-induced ions like iron ions, likely from contact with metallic objects. [47,48]. Foxing is a particular type of surface contamination on paper that appears as rusty-red, irregularly shaped spots. The foxing was removed using a solid pulse device Nd:YAG laser device. A quantitative evaluation technique based on monitoring the RGB feature of laser paper cleaning was developed and evaluated to determine its effectiveness. The invention of the selective laser cleaning technique for papersand books is another significant result [49,50]. In a study by Pilch et al. [51], laser removal of foxing stains was conducted at 532 nm following the sterilization of rag paper with ethanol. According to Petronic et al. [52], Nd:YAG lasers at two wavelengths, 532 nm (green) and 1064 nm (infrared), have been considered as a tool in cleaning iron stains. Rudolph et al. [53] found that using second harmonic green light at a wavelength of λ= 532 nm for laser cleaning below the ablation threshold produced the most promising results on virgin paper. This method did not cause discoloration or other visible changes, and no detectable chemical changes were observed. The paper surface layer was damaged by laser cleaning at a wavelength of 1064 nm, but at 532 nm, it did not completely remove the iron stains. A laser operating at 552 nm is included in the suggested effective cleaning process for historical materials in order to remove stains [52-55].

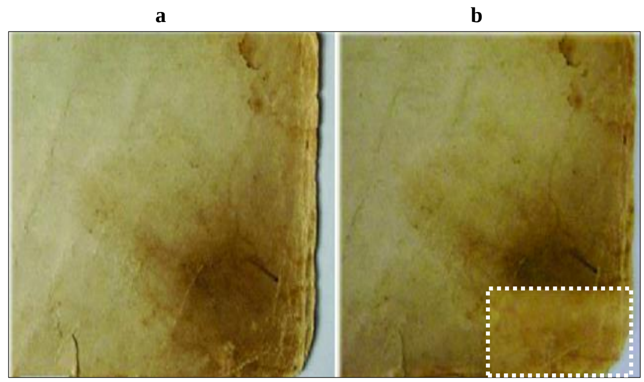

Figure (5) surface of a handwritten paper book sheet; **a.** before cleaning, and **b.** after laser cleaning [44].

4.4. *Plasma cleaning*

Plasma can be described as a gas that is at leastpartially ionized and forms a complex mixture of various components, including neutral species, charged particles, radicals, radiant heat, and UV photons. Plasma is classified depending on its temperature into thermal and non-thermal plasma [56]. To generate cold plasma, energy must be provided to the gas, and electrical power sources have proven to be significant in practical applications. Particles inside the plasma have a very brief lifetime due to energy loss from the collision process, and consequently, energy needs to be continuouslyprovided for plasma application. Cold plasma generation can be performed at lower pressureconditions and/or atmospheric pressure [57,58]. Plasma cleaning is often achieved in a chamberor vacuum chamber, fig. (6). The air inside the chamber or housing is pumped out before the gas is let in. The gas then circulates in the low-pressure environment. This is done before any energyis applied [58]. It is essential to note that plasma cleaning is carried out at low temperatures, making it possible to easily process heat-sensitive materials. There are also many plasma systems that operate at atmospheric pressure in ambient air. In general, cold plasma, suitablefor cultural heritage cleaning, is intended to excite gases at reduced atmospheric pressure using radiofrequency energy [58,59]. However, for cleaning purposes, chemical etching, activation, and excision can be utilized. Ablation is the process of removing stains by the evaporation of surface materials. Plasma ablation implies the energetic bombardment of electrons and ions to mechanically remove surface impurities. The abrasion process involvesthe mechanical cleaning of surface stains by the vigorous bombardment of ions and electrons.The abrasion process only wears away the outermost molecular materials of the stain layers.Argon plasma is commonly used because of its chemical inertness and remarkable ablation efficiency on paper surfaces [58,59]. Particles also interact with the object being processed and can also be accelerated to the surface. In addition, all the species presented (electrons and protons – apart from the elementary particles) have internal excitement energy that contributes to the reduction of the energy barrier required for the initiation of the reactions mentioned above. The particles reach the surface of the object to be treated together, so it's not possible to accurately detect which particle has the highest processing efficiency [58-60]. Văcar et al. [61] found that plasma treatment does not alter the structure of paper fibers, making it suitable for preserving archival or paper documents. By adjusting processing parameters like pressure, flow rate, time, and power, positive effects on paper stability can be achieved. It was possible to increase paper durability and stability by up to 20% [59,62]. Vizárová et al. [63] demonstrated the decontamination effects of ADRE plasma on various filamentous fungi commonly found in archives and libraries. Complete loss of vitality in fungal species was observed 10 to 15 minutes after treatment. The effectiveness varied based on the paper type, the gas/air used, and the specific fungal species.

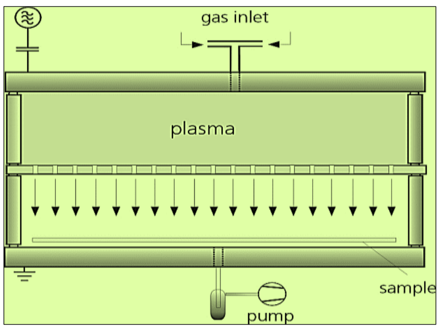

Figure (6) schematic view of the specially designed after-glow plasma treatment chamber [59].

5. Analysis and Investigations

There is no doubt that the removal of iron rust from paper artifacts is an essential matter thatdepends on the cleaning methods used. Examinations are used to identify the general appearance of the paper object, such as deterioration aspects. They can be used to determine the state of deterioration or preservation of historical papers [64]. Analysis processes are used to identify the chemical composition of the artifacts. They are also used to evaluate materials and conservation methods. Regarding iron rust, analysis and preservation are significantly important to identify iron compounds or other materials for removing iron rust from paper artifacts [64]. The following methods of examination and analysis can be utilized for these objectives:

5.1. *Visual assessment*

The primary method for determining various stains and the extent of paper deterioration is accurate note-taking. Figueira et al. [65] used an approach that depends on the visual assessment of paper collections by the critical eye and digital imaging under variousilluminations to record the iron rust and foxing stains found on paper collections. Additionally, visual observation can be used for the initial assessment with digital images under various lighting conditions on iron removal/reduction to evaluate the removal of all visually detectable rust residue in the treated paper [8,66].

5.2. *Light microscope*

The optical microscope can be utilized extensively in this process to provide more details about the paper surface and different stains, such as iron rust. Additionally, it is significant todetermine the most effective analytical techniques that should be applied to determine iron stains or the use of cleaning methods and materials. Koochakzaei & Gharetapeh [67] used a light microscope to detect foxing stains and observe the yellow-brown spots in foxing.

5.3. *pH value measurement*

The pH meter is used to measure the pH value of the iron-rusted papers. It identifies the impact of the iron rust on the pH value of paper objects, particularly when using cleaning materials on the surface of the paper. The pH values before and after treatment showed interesting results and were used to monitor the changes in the solutions [8,63]. Parfenov et al. [44] studied how rust and dirt can impact the pH value of paper objects, either reducing or increasing it.

5.4. *SEM-EDAX*

SEM is utilized to observe the surface morphology of papers and evaluate cleaning methodsand materials. It is used to determine the composition of stains from a chemical point of view and to explain aspects of degradation observed on the surface of paper objects. Moreover, it aimsto assess the effectiveness of cleaning materials and methods used to remove stains, fig. (7) [68]. Ciofini et al. [48] found that the EDX spectrum following laser cleaning of darker rusty-red stains exhibited a notable decrease in all components introduced during the papermaking process, with a complete absence of Fe elements.

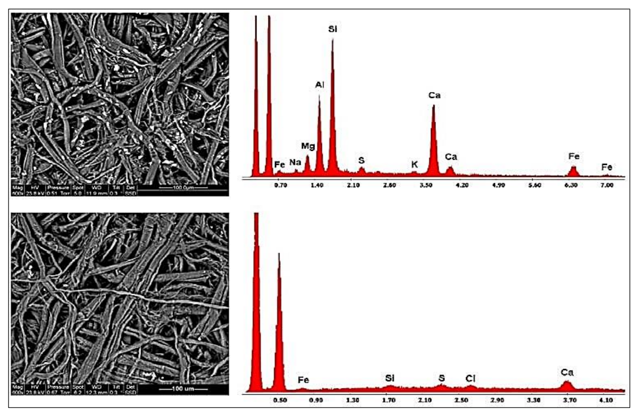

Figure (7) backscattered electron (BSE) images and an energy dispersive x-ray (EDX) spectrum of a nonfluorescent rust stain before (top) and after laser treatment (bottom) [48].

5.5. *Change of color*

Spectrophotometry is a non-invasive technique for measuring the amount of light transmittedor reflected through materials at various spectral wavelengths. It was developed by combining this analytical method with the widely accepted colorimetric CIE-L*a*b* systemby CIE (Commission Internationale de l'Eclairage). Color can be described numerically in three dimensions (L*, a*, b*). (L*) determines the brightness, with white reaching a maximum value of 100 and black a minimum value of 0. (a*) represents the coordinates of green (negative value) and red (positive value). (b*) represents the coordinates of blue (negative value) and yellow (positive value). The color difference rating is determined using the CIE1976 color difference formula L*a*b*

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}.$$

Where the values ΔL*, Δa*, and Δb* are the differences between related values assigned. These methods can be used to evaluate cleaning materials and methods before and after cleaning [69]. Ciofini et al. [48] found that changes in the colorimetric coordinates a* and b* offer valuable insights into the color changes resulting from laser cleaning. The a* and b* coordinates measured before and after removing rusty-red foxing stains were compared, showing a significant reduction in the range of values after laser treatment fig. (8).

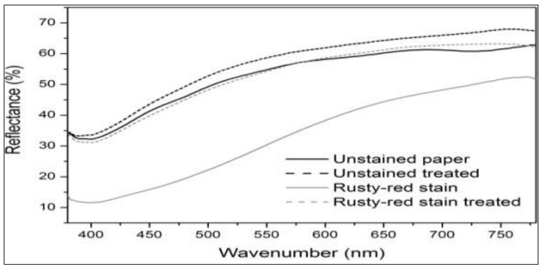

Figure (8) the unstained and stained areas before and after laser cleaning of rust stains on the left, with a corresponding shift in the colorimetric coordinates a* and b* on the right [48].

5.6. *FTIR spectroscopy*

FTIR is utilized to monitor chemical properties and distinguish changes that occur in the papers after cleaning. FTIR is also used to analyze iron rust and distinguish between differentstains. It can also be utilized to identify the effects of iron rust on paper components [70,71]. Parfenov et al. [44] used a 10 mm diameter diaphragm to define the measurement area, which encompasses common paper stains such as silicate glue residue, rust, moisture, grease, dirt, and more, fig. (9).

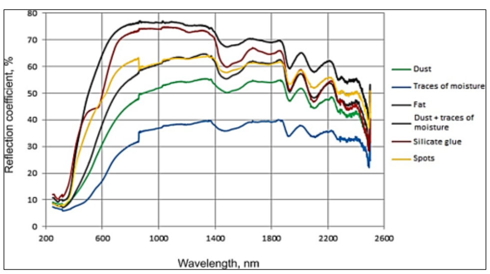

Figure (9) the reflectivity coefficient of paper with contaminants plotted against laser radiation wavelength [44].

5.7. *X-ray diffraction (XRD)*

X-ray diffraction is generally used to determine the chemical composition of crystallized inorganic compounds and the degree of crystallization in organic compounds. This method is also used to analyze the composition of rust products, which is important for choosing cleaning materials and methods for iron rust removal [72-74]. Nakamura et al. [2] have used XRD to analyze the rust stains, fig. (2). The main component of iron rust is found to be β-FeOOH, fig. (10).

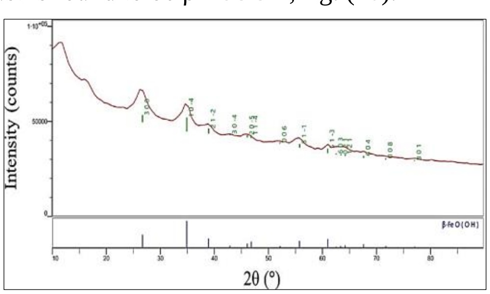

Figure (10) XRD analysis results of rust stains created on a slide glass [2].

5.8. *Investigation of the surface topography and roughness using AFM*

Atomic force microscope (AFM) is a proposed method for imaging most cultural heritage documents. Atomic force microscopy is an instrument used in cultural heritage to study surface topography. The atomic force microscope offers numerous advantages over traditional microscopy methods. Itinspects the paper and measures it in three dimensions: X, Y, and Z, obtaining ultrafine 2D and 3D images. Atomic force microscopy measures the surface roughness of cleaned and uncleaned papers [75,76]. Li et al. [77] used AFM to measure the surface roughness of un-foxed and foxed areas, fig. (11). AFM was employed to assess the effects of cleaning methods and materials on surface morphology.

a **b**

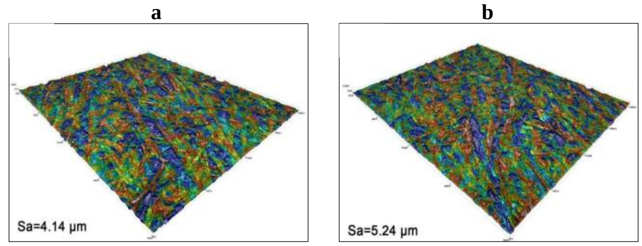

Figure (11) 3D images of **a.** the un-foxed area at 10-x, **b.** foxed area of the manuscript at 10-x [77].

5.9. *EDXRF*

Energy dispersive X-ray fluorescence (EDXRF) is accurate in determining the ratios of elements and is a mapping analysis techniquethat must be used for quantitative analysis. It allows for non-destructive multi-element analysis for every element with an atomic number greater than 13 (or even lower in a vacuum) over an extensive concentration range. EDXRF is used to detect particles on contaminated paper surfaces and to detect any remaining particles after the cleaning process [78-80].

6. Conclusions

Iron rust is a significant factor in the deterioration of paper objects. Initially, discoloration is visible on metalclips or staples, turning them brown due to rust. This discoloration may spread to the archival object, but the degradation is minimal at first. If the artifact shows significant discoloration around the metal clips and is further damaged by rough handling, the deterioration is moderate, sometimes leading to holes in the affected areas. Different cleaning techniques have their pros and cons, and the choice of method depends on the object'scondition, size, and the nature of the rust. Analysis and examination are essential for identifying, describing, and determining the composition of iron rust, as well as for evaluating cleaning methods, especially in experimental studies.

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