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Plasma Techniques for Cleaning Paper-Based Artworks: A Comprehensive Review

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Abstract

Paper-based artworks are susceptible to deterioration over time due to various factors such as exposure to light, humidity, and pollutants. Stains on paper can further accelerate this deterioration process and compromise the integrity of the artwork. This study aims to provide a comprehensive understanding of different methods for stain removal using plasma technology. Plasma treatment involves the use of ionized gas to modify the surface properties of materials. In the context of paper conservation, plasma techniques can be used to selectively remove stains without damaging the underlying paper substrate. These techniques include atmospheric pressure plasma, low-pressure plasma, and cold plasma treatment. Atmospheric pressure plasma is a non-thermal plasma treatment that can effectively remove stains from paper surfaces without causing thermal damage. Low-pressure plasma treatment involves the use of vacuum chambers to create a controlled environment for stain removal. Cold plasma treatment utilizes low temperatures to prevent heat damage to the paper while effectively removing stains. Overall, plasma techniques offer a safe and efficient method for the removal of stains from paper-based artworks, preserving their aesthetic and historical value for future generations.

Keywords: paper-based artworks, stains, cleaning, Cold plasma, classification of plasma.

1. Introduction

Historical paper-based artworks play a crucial role in museums and libraries as they provide a tangible connection to the past. These artworks, such as manuscripts, maps, and prints, offer a glimpse into the history, culture, and artistic practices of different time periods. They serve as valuable primary sources for researchers, historians, and art enthusiasts, allowing them to study and appreciate the craftsmanship and creativity of past generations. Historical paper is typically made from plant fibers, such as cotton or wood pulp, which are processed and formed into sheets. The chemical composition of historical paper can vary depending on the type of plant fibers used and the manufacturing process [1,2]. The historical paper artworks are often susceptible to staining, which can affect their readability and preservation. Different types of stains, such as water damage, mold, ink, iron corrosion, etc. can have varying effects on historical papers [3,4]. Water damage (Figure 1 a, b, c) is a common issue that can cause papers to become discolored and wrinkled. This type of stain can weaken the paper fibers and lead to deterioration over time [5]. Mold stains, on the other hand, can be particularly damaging as they can spread quickly and cause irreversible damage to the paper [6,7]. Ink stains, while less harmful than water and mold stains, can still impact the readability of the text and detract from the overall appearance of the document [6,8].

In the past, pressure-sensitive adhesive tape (PSAT) was frequently used to repair torn documents and books, resulting in deformed and damaged books. PSAT is also challenging to remove [9]. (Figure 2).

In order to preserve historical papers, it is important to address stains promptly and with care. Different stains may require different treatment methods, such as gentle cleaning techniques or specialized restoration processes [6]. By understanding the effects of various stains on

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historical papers, conservators can work to protect these valuable documents for future generations.

Historical paper conservation poses unique challenges due to the delicate nature of the materials involved. While various cleaning techniques such as mechanical, chemical, wet, enzymes, and laser methods are available, each comes with its own set of disadvantages [10,11].

Mechanical cleaning involves physically removing dirt and debris from the paper surface using tools like brushes or erasers. However, this method can be abrasive and may cause damage to the paper fibers, especially if not done carefully [9,12].

Chemical cleaning uses solvents or cleaning agents to dissolve or break down contaminants on the paper. While effective, these chemicals can be harsh and may alter the paper's original appearance or composition if not used correctly [13,14].

Wet cleaning involves immersing the paper in water or a cleaning solution to remove dirt and stains. This method can be risky as excessive moisture can weaken the paper and lead to irreversible damage like warping or mold growth [15,16].

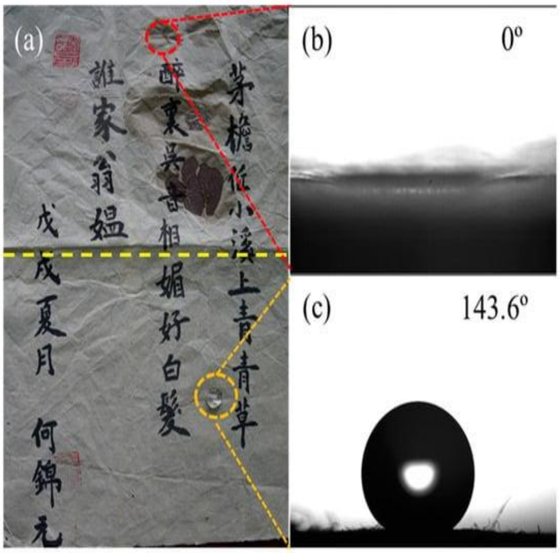

Fig. 1. shows water drops on the surfaces of the untreated (upper region of the dashed bright yellow line) and treated paper relics (lower region of the dashed bright yellow line) (a), as well as the measured water contact angle of the untreated (b) and treated (c) paper [5].

Enzyme cleaning utilizes biological enzymes to break down organic stains on the paper. While gentle and effective, this method requires precise control of enzyme concentration and application time to avoid over-treatment [17-19].

Laser cleaning uses focused beams of light to vaporize contaminants on the paper surface. While precise and non-invasive, this technique can be expensive and may require specialized equipment and expertise [20].

In conclusion, while these cleaning techniques offer solutions for preserving historical paper, it is essential to consider their potential drawbacks and limitations to ensure the safe and effective conservation of valuable artifacts.

One of the key techniques used in the cleaning and restoration of historical paper is plasma cleaning. Plasma cleaning is a non-invasive and highly effective method that can remove dirt, stains, and other contaminants from delicate paper without causing damage. In addition to its gentle nature, plasma cleaning is also highly efficient. It can remove a wide range of contaminants, including dirt, mold, and pollutants, without leaving any residue behind. This ensures that the paper is thoroughly cleaned and restored to its original condition [21,22].

Furthermore, plasma cleaning is a versatile technique that can be used on a variety of historical paper materials, including manuscripts, maps, and artwork. Whether the paper is made from parchment, vellum, or other materials, plasma cleaning can effectively clean and restore it without causing any damage [23].

Plasma is the fourth state of matter, a gas that is partially ionized and consists of a mix of neutral species, charged particles, UV photons, and radicals [21,24]. It can be classified into thermal and non-thermal plasma based on temperature. Thermal plasma is almost fully ionized with temperatures exceeding 15,000 K [21,25,26], while non-thermal plasma is partially ionized with varying temperatures among particles, including room temperature for ions and neutral species and a few thousand Kelvin for electrons [27,28-30].

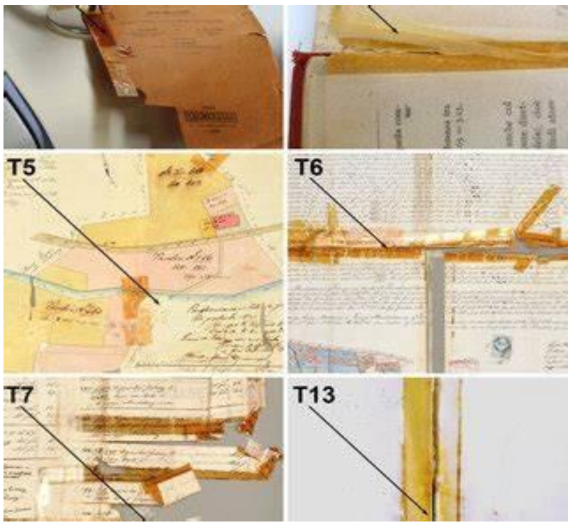

Figure. 2. Dark brown staining along the split spine fold of paper caused by pressure-sensitive adhesive tape (PSAT) on some of the maps and book papers [9].

The application of electric fields (such as alternative current (AC), direct current (DC), pulsed, and microwave (MW), radio frequency (RF)) to gas is a common method for generating plasma in the laboratory. This process increases the kinetic energy of background electrons, leading to more collisions between electrons and free electrons, resulting in the ionization and excitation of the gas [21,31,32]. The chemistry that takes place in plasma is highly complex and involves a wide range of elementary reactions [33, 34]. Reactions in plasma volumes can be categorized as heterogeneous or homogeneous. Homogeneous reactions occur between substances in the gas phase due to inelastic interactions between heavy substances and electrons or interactions between heavy substances. Heterogeneous reactions, on the other hand, occur between the solid surface immersed in the plasma species or when exposed to the plasma [35,36].

Plasma cleaning is a novel method for cleaning paper surfaces without altering their bulk properties. The effectiveness of plasma cleaning at these interfaces depends on the plasma system configuration, operating parameters, and source gas.

Plasma cleaning is a process that involves using energetic plasma generated from gases to remove contaminants and impurities from a surface [37,38]. Specific gases like argon, helium, hydrogen, oxygen, and atmospheric gases can be used to create the plasma [39,40].

The surface is exposed to the discharged plasma gas, which effectively cleans the surface by rubbing it thoroughly. This technique is useful for removing dust, rust, contaminants, and impurities that accumulate on surfaces during processing, manufacturing, or exposure. One of the advantages of plasma cleaning is that no residue is left behind on the surfaces. Plasma cleaners are commonly used before gluing to remove tough residues and activate the surface for better bonding. Additionally, plasma cleaning can be used to clean cultural heritage materials and objects effectively [41-43]. Below in Table 1 is a summary of previous studies confirming the efficiency of plasma in cleaning various stains found on paper works.

Table 1: Summary of Previous Studies Confirming the Efficiency of Plasma in Cleaning Various Stains on Paper Works.

Authors/ Year	Previous Work Summary:
Văcar, et al. (2023) [44].	Use cold atmospheric plasma as an appropriate technique to treat paper damage caused by cellulolytic bacteria. The results showed efficiency in cleaning papers without altering the structure of the paper fibers.
Jiao, et al. (2023) [45].	Research shows that reactive nitrogen species, reactive oxygen species, ozone, hydroxyl radicals, electric fields and peroxide radicals are the active ingredients in the decontamination of paper relics.
Vizárová, et al. (2021) [46].	The decontamination impact was observed on all filamentous fungi. Complete loss of vitality with ADRE plasma was observed 10 to 15 minutes after treatment. Differences were noted based on the type of paper, the species of filamentous fungi, and the working gas/air used.
Tiňo, et al. (2019) [21].	ADRE plasma was able to effectively disinfect various types of paper colonized by *P. chrysogenum* and the disinfection efficiency depended on the type of paper as well as the plasma treatment conditions.
Yan, et al. (2019) [5].	Atmospheric pressure plasma polymerization of the precursor hexamethyldisiloxane (HMDSO) was investigated on paper artifacts. These nanoparticles offer significant water resistance properties with a large static water contact angle and a smaller rolling angle, to protect the papers from water penetration.
Patelli, et al. (2018) [47].	A new plasma torch has been developed with a redesigned to overcome the current limitations of atmospheric plasma devices. This research will be presented on removing epoxy coatings and cleaning daguerreotypes, etc.
Hanus, et al. (2017) [48].	The advantage of applying plasma techniques can be an increase in labor productivity in individual preservation technological treatments such as stabilization, cleaning, i.e. prolonging the life of artifacts and sterilization.
Ioanid, et al. (2012) [49].	Microbiological analysis results showed complete cessation of bacterial growth and multiplication after 6 minutes of corona discharge treatment and after 15 minutes of treatment in HF plasma. Therefore, the results show that corona discharge decontamination treatment is more effective than HF cold plasma treatment.
Vohrer, et al. (2001) [23].	The main objective of this work was to eliminate bacterial contamination while increasing paper durability through plasma-based processing. This study demonstrates the fungicidal and bactericidal effects of residual plasma treatment. However, consideration should be given to optimizing for different types of microorganisms and paper types.
Banks, et al. (1998) [50].	An atomic oxygen source operating at atmospheric pressure, using a mixture of helium and oxygen, has been designed to produce a highly efficient atomic oxygen beam for oxidizing soot deposited on paper surfaces.

A critical review of the use of plasma cleaning techniques has been summarized in Table (1) to identify research trends related to cold plasma-developed treatment methods for cleaning techniques. This review article highlights and provides detailed information on the benefits of using cold plasma to clean and decontaminate cultural heritage papers. Plasma cleaning reduces time and has a minor negative effect on the paper materials. Plasma treatment offers a promising alternative to traditional physical methods for various stain removal from paper materials.

2. Plasma classification

Plasmas can be classified based on various characteristics such as ionization, density, temperature, size, and model approximations. This classification results in different types of plasmas.

2.1. Thermal Plasma (Hot Plasma):

Thermal plasma is a fully ionized gas created at high pressure (>10 kPa). It is known for its high temperatures, energy flux, radiation emission, density, and equilibrium between the temperatures of heavy particles ($T_e = T_i = T_n = 104$ k), where T_i is the ion temperature, T_n is the neutral gas temperature, and T_e is the electron temperature) [25,51,52].

2.2. Non-Thermal Plasma (Cold Plasma):

Non-thermal plasma is a partially ionized gas with low energy density and a significant difference between the temperatures of electrons and heavy particles ($T_e > T_i = T_n$) [41,53].

3. Plasma cleaning processes

Plasma cleaning involves the use of an activated stream of ions and atoms to break down organic contaminants, acting like a molecular sandblast. This process can volatilize contaminants, producing gases like CO_2, hydrocarbons, and water vapor with traces of carbon monoxide [54]. The interaction between plasma-generated species and solid surfaces leads to surface modification without affecting bulk properties. The effectiveness of plasma cleaning depends on operating parameters, system configuration, and source gas. Plasma can be used for cleaning, sterilization, activation, etching, and cross-linking of materials like papers [21,55].

The O– species further generate oxidizing radicals such as $HO_2^{\bullet-}$, $OH^{\bullet}$, $RO^{\bullet}$, $RO_2^{\bullet}$ which will eventually degrade the stains on the paper [56].

$e^-_{cb} + O_2 \rightarrow O_2^-$ [56]

$RCOO + h_{yb} \rightarrow R^{\bullet} + CO_2$ [56]

Cold plasma (CP) is an advanced oxidation process used to remove organic contaminants [21] deposited on surfaces. In oxygen plasma cleaning, the organic compounds containing hydrogen and carbon react with oxygen to form volatile products like H2O and CO_2, which are then removed from the surface substrate by gas flow.

$C_xH_y + O^- \rightarrow CO_2 + H_2O$ [57]

The choice of plasma chemistry depends on the stability and volatility of the corrosion product. Different types of hydrides, halogens, and methyl compounds can be used based on their volatility. For elemental materials, various options are available to customize efficiency and corrosion characteristics for specific applications.

$Si_{(solid)} + 2F_2 \rightarrow SiF_{4\,(gaseous)}$ [57]

Cold atmospheric plasmas are typically generated using noble gases such as helium and argon, either alone or in combination with other molecular gases like nitrogen and oxygen. Helium and argon have lower breakdown voltage characteristics at atmospheric pressure, making them efficient for igniting and sustaining plasma discharges. By adding helium and argon to other active gases, lower voltages can be used to produce stable plasma discharges and increase the formation of reactive species [49,56].

The active oxygen and nitrogen species produced in plasma play a crucial role in many treatment processes. Oxygen plasma, even in after-glow conditions, does not cause significant paper degradation [23,58], although it may slightly reduce mechanical properties [58,59]. However, subsequent cleaning with hydrogen plasma can restore the original tensile strength. This is important information as oxygen plasma is more effective in inactivating bacterial contamination compared to hydrogen plasma. Gases containing oxygen are generally oxidizing and highly effective for cleaning purposes. However, it is essential to monitor their potential decomposition effects on the treated material due to their oxidizing nature [5, 58].

Hydrogen was selected for its reducing potential as part of the natural transformation of cellulose involves oxidation. Hydrogen plasma cleaning reduces the hydroxyl groups on the cellulose surface, resulting in materials with low polarity, low molecular weight, and significant water resistance properties. It was found that the tensile strength decreased significantly after direct oxygen plasma cleaning. In contrast, treatment with hydrogen plasma showed the least deterioration [5,58]. Additionally, using hydrogen plasma under glow conditions in a specially designed plasma treatment chamber enhances mechanical properties under pressure, as demonstrated by adsorption measurements of tensile strength on the treated samples [5,21,58].

By introducing new chemical groups, various plasma gases can induce different effects on the paper surface. For instance, plasma enriched with oxygen (O_2) can generate new C=O or O-C-O groups on cellulose fibers, whereas plasma infused with nitrogen can form C=O or O=C=NH groups, resulting in the formation of a hydrophobic layer [49].

3.1 Decontamination/Sterilization

Plasma disinfection treatment is increasingly being used for the disinfection and sterilization of medical devices. Plasma techniques offer simultaneous cleaning and disinfection, making them suitable for disinfecting organic materials and objects that are often colonized by harmful microorganisms [57,31]. Plasma sterilization works differently due to the presence of active agents such as free radicals and UV photons [21].

A key consideration in plasma sterilization is the balance between ultraviolet and reactive species like atoms and radicals. Ultraviolet photons are mostly absorbed by the surrounding gas at atmospheric pressure, whereas at reduced pressures below 10 torr, oxygen becomes the primary deactivating agent, generating oxygen atoms that can be corrosive [60,61]. The roles of radicals and ultraviolet photons at reduced pressures have been studied [46,62], but this has not been extensively explored at atmospheric pressure.

Ultraviolet photons emitted from cold plasma can cause dimerization of thymine dimers in DNA, inhibiting bacterial replication. They can also damage bacterial DNA spores [63].

The selection of plasma chemistry is determined by the stability and volatility of the corrosion product. Different hydrides, halogens, and methyl compounds can be utilized depending on their volatility. For elemental materials, there are several options to tailor efficiency and corrosion properties to suit specific applications [46].

Fungal decontamination is influenced by the atmosphere created by plasma discharge and the production of reactive oxygen and nitrogen species (RNOS). Different gases have varying effects on different types of paper and microorganisms. The common hypothesis is that microbial inactivation by air plasma is due to oxidative damage caused by stable active species like hydrogen peroxide and ozone, as well as short-lived reactive oxygen species such as atomic oxygen and hydroxyl radicals. Hydroxyl radicals are formed during plasma discharge in humid atmospheres or on moist substrates and can react with organic materials, leading to chain oxidation and damage to cell membranes and other cellular components [21,46].

3.2. Plasma surface activation

Plasma surface activation involves using plasma gas at atmospheric pressure to modify the chemical functional groups on surfaces such as nitrogen, oxygen, and hydrogen. This process replaces the surface polymer groups with chemical groups from the plasma gas, resulting in a cleaner surface free of organic contaminants. Additionally, plasma treatment alters the surface topography, reduces metal oxides, and deposits functional chemical groups. By destroying the weak surface bonds of the polymer and replacing them with more reactive hydroxyl, carboxyl, and carbonyl groups, the activation process changes the chemical behavior and surface properties [21,64].

3.3. Ablation

Ablation is the process of removing a surface by evaporating the surface materials. When modifying surfaces with plasma, three main effects are usually observed.

1. Functionalization: This process creates covalent bonds to enhance the adhesion of additional coatings.

2. Cross-linking: This systematically strengthens the upper surface layer.

3. Surface abrasion: This can be utilized to clean surfaces [65,66].

Plasma ablation removes surface contaminants by bombarding them with energetic ions and electrons. The contaminant layers often contain weak C-H bonds. The ablation process destroys the weak covalent bonds of polymer contaminants through mechanical bombardment and subsequent surface contamination, which undergoes repeated chain fragmentation until their molecular weight is low enough to evaporate in a vacuum. Abrasion only affects contaminants and the surface molecular layer of the base materials.

Argon is often used for ablation due to its high ablation efficiency and inertness to the surface material [64,66].

3.4. Crosslinking

Plasma treatment with inert gases can create chemical bonds between polymer chains, a process known as cross-linking. This can enhance the chemical and abrasion resistance of materials.

3.5. Coating Deposition

During plasma processing, a thin polymer layer is deposited on the substrate surface through gas-phase polymerization. The properties of these thin films depend on the gas and process parameters employed.

4. Mechanism of Plasma Cleaning

Plasma creates ions, electrons, and free radicals that interact with surfaces, leading to three key phenomena for surface cleaning: etching, heating, and spraying. The synergy of these plasma-driven processes results in optimal cleaning effectiveness [57,67].

4.1. Plasma Cleaning by Heating

Plasma cleaning by heating is a straightforward method. Surfaces in a plasma environment become heated mainly due to ions and electrons bombarding them and plasma radiation. Applying a positive or negative voltage bias on the substrate compared to the plasma potential can enhance the energy flow of ions and electrons [68]. Mild heating is effective in removing loosely bound contaminants, and utilizing the heat generated by plasma electrons can enhance the cleaning efficiency.

4.2. Cleaning by sputtering

Sputter cleaning is a commonly used process that involves applying a voltage between the object being cleaned and the plasma [69]. The effectiveness of sputtering atoms depends on the surface area and type of contaminant present, although all atoms can be sputtered. However, sputtering is not selective and may not completely remove contaminants [57]. Additionally, sputtering can potentially damage the base material and create defects, especially in the final stages when only isolated contaminant pools remain. Despite these drawbacks, plasma sputter cleaning is still widely used in cases where plasma etching and heating are not sufficient, such as in technological processes that require high levels of cleanliness [57,69].

4.3. Cleaning by etching

In the plasma etching cleaning process, free radicals or atoms in the plasma chemically interact with surfaces. Initially, these substances adsorb onto the surface depending on chemical affinity and surface temperature. The adsorbed substances can then interact with surface atoms and molecules to create products, or they may desorb without reacting. Reaction products that evaporate can desorb into the gas phase and be pumped away. The gas mixture chosen for etching (plasma chemistry) depends on the stability and volatility of the etching products [57].

5. Plasma sources

Cold plasma is commonly generated in the laboratory using a low-pressure electroluminescence process with different electric field frequencies: direct current (DC), acoustic frequency (AF) (typically between 10 to 50 kHz), radio frequency (RF, often 13.56 MHz), and microwave frequency (MW, mainly 2.45 GHz) [70-72] (Figure 3).

Plasma cleaning utilizes various plasma sources, such as direct current (DC), microwave glow discharge (MW), radio frequency (RF), dielectric barrier discharge (DBD), plasma jets, and confined glow discharge systems. Low-frequency sources are cost-effective and easy to operate. The choice of the plasma source depends on factors like economic cost. In each case, the characteristics of the plasma source that will have the best impact on the surface and the optimal processing conditions (time, power, gas usage, etc.) need to be determined. Plasma sources can be classified into two types: low-pressure sources operating under vacuum and high-pressure sources that work at atmospheric pressure.

5.1. Low-pressure (vacuum) sources

Organic materials that are heat-sensitive, such as paper, wood, leather, and parchment, cannot withstand exposure to plasma at high temperatures. Therefore, it is crucial to focus on systems that generate plasma at or near room temperature to prevent thermal degradation during processing.

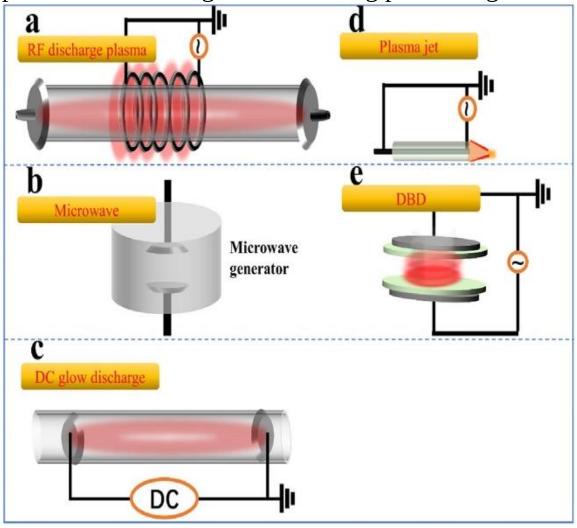

Fig. 3. Several types of plasma setups. (a) RF plasma, (b) MW plasma, (c) DC glow plasma, (d) cold plasma jet, (e) DBD cold plasma [72].

5.1.1. RF plasma

RF discharge sources are commonly used to clean papers. Vertical and horizontal parallel plate reactors are the most common setups, where RF power is capacitively coupled. When the paper is placed on the ground electrode, it is exposed to energetic particles generated at the source electrode. The energy of bombarding ions can be adjusted by changing the electrode surface ratio when the object is on the powered electrode. Large wafers can also be cleaned in a parallel plate induction reactor with inductively coupled radio frequency (RF) power, which provides better cleaning conditions compared to capacitive coupling [57].

An inductively coupled radio frequency (RF) discharge creates weakly ionized oxygen plasma in a discharge chamber. The RF generator operates at a frequency of 27.12 MHz and about 500 watts. The plasma allows for even treatment of paper within the reactor chamber. The pressure is set to 30 Pascals, and treatment times range from 10 to 60 seconds. Documents are processed on a glass table in a plasma reactor (Figure 4) [73]. Plasma treatment typically modifies only the first few nanometers of a surface, selectively etching the organic coating components of porous paper and opening the porous microstructure several micrometers deep. This effect is stable over time, allowing plasma treatment to improve the properties of paper [73].

5.2. Atmospheric-pressure plasma sources for cleaning

Atmospheric pressure plasma cleaning does not require expensive vacuum equipment, but it does come with its own set of challenges. To achieve effective cleaning, it is essential to have clean air and completely remove cleaning materials. This can be achieved by using sealed volumes and rapid gas flows to minimize surface recontamination.

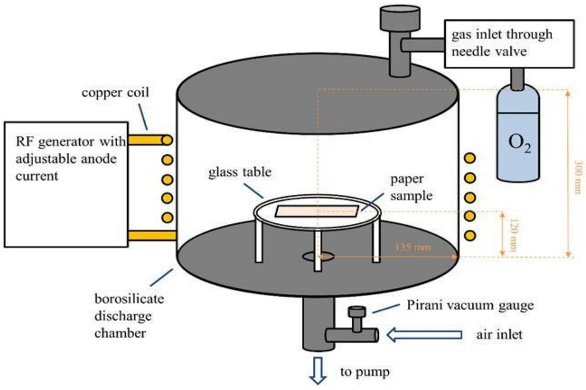

Fig. 4. Schematic showing the plasma reactor utilized for the treatment of papers [73].

Atmospheric pressure plasma used for surface cleaning purposes is typically generated in gas mixtures containing argon, helium, air, neon, nitrogen, dioxygen, and hydrogen. Metastable species like N_2 and He play a crucial role in stabilizing the discharge, forming plasma, and destroying contaminants [57]. The specific gas mixtures used depend on the cleaning techniques employed. For example, the presence of a small percentage of dioxygen in the plasma can aid in oxidizing organic compounds, leading to the production of carbon dioxide, carbon monoxide, and fragments of organic pollutants during decomposition. It is important to remove these fragments to prevent recontamination. Each gas mixture requires a customized treatment protocol to achieve optimal cleaning results.

However, the requirements for rapid gas flow, clean environments, particle removal, and electrode cooling can increase the costs and complexity of atmospheric pressure plasma cleaning systems [74]. Additionally, certain gases like O_2, which are effective in removing lubricants from paper, may lead to the undesired formation of oxides on cleaned surfaces [21]. Careful consideration of gas mixtures and treatment protocols is essential to ensure efficient and effective cleaning processes.

5.2.1. Atmospheric Pressure Glow Discharge (APGD)

Atmospheric Pressure Glow Discharge (APGD) plasma is generated by applying a relatively low voltage (~200 V) at a high or very high frequency (2 to 60 MHz) between symmetrically flat or bare metal electrodes, separated by just a few millimeters [75,76]. The higher frequency used in APGD plasma allows for much higher power densities (up to 500 W/cm3) despite the absence of a dielectric barrier on the electrodes. Typically, applying a voltage between bare metal plates would result in a high-current, hot plasma arc, but in the case of APGD plasma, using helium as ~99% of the generation gas prevents arcing and produces a large volume of non-thermal yet dense plasma rich in the chemical species required for surface modification [77].

Atmospheric Pressure Plasma-Enhanced Chemical Vapor Deposition (AP-PECVD) has been successfully employed to alter the surface chemistry of cellulose-based substrates [78].

5.2.2 Dielectric Barrier Discharge (DBD) Plasma

A DBD source generates a non-equilibrium plasma that maintains a relatively low gas temperature. Dielectric barrier discharge has been extensively studied and can be easily adapted for surface cleaning. The energy needed to create a DBD is typically supplied by an alternating current (AC) power source with a frequency ranging from 10 to 10^4 Hz. DBD devices usually consist of two parallel planar electrodes, with one or both coated with a dielectric material (Figure 5) [57]. When cleaning surfaces of dielectric materials, such as photographs contaminated with soot, the material being cleaned can serve as a dielectric barrier. The object to be cleaned can be placed on one of the electrodes, with a dielectric material covering the second electrode if treating a paper surface. DBD exhibits a filamentary nature, where discharge currents or channels form at random locations along the dielectric due to charge accumulation on the surface [79].

Plasma treatment is considered an environmentally friendly alternative to traditional cleaning methods as it reduces the risk of damage to delicate surfaces and allows for precise control [80,81]. Unlike chemical processes, plasma treatment is completely non-toxic, non-invasive, and eco-friendly [82].

5.2.3. Atmospheric Discharge with Runaway Electrons (ADRE) Plasma

ADRE plasma is a low-temperature plasma formed at atmospheric pressure. It involves the generation of fast electrons with energies ranging from 20 to 350 keV in the space between the electrodes and behind the anode. This rapid electron flow creates a bright light across the entire surface behind the anode. An increase in voltage pulse by two to three times results in a noticeable change in radiation between the electrodes [83].

The ADRE generator has been utilized for treating thick wood. This system produces a high-energy volumetric corona discharge at room temperature, making it suitable for treating flat 2D objects and reliefs that can be several centimeters high. ADRE plasma maintains its stability in the air and does not cause significant alterations to gelatin layers when used for cleaning. These techniques are recommended for bacterial decontamination and image cleaning, showing promise in these applications [83].

Plasma cleaning does not significantly alter the main chemical structure of paper. A study using

ATR-FTIR spectroscopy found no changes in the material's chemical structure [83].

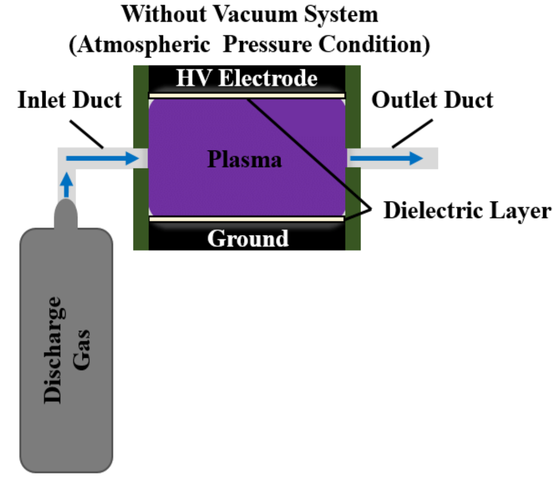

Fig. 5. The basic structure of a DBD reactor operating under

Although no quantitative data processing was performed, the FTIR spectra showed a reduced contribution of OH and CH to the plasma-treated paper compared to the untreated paper. One possible explanation is that the treatment resulted in the removal of the outer layer from the fibers surface [84]. (Figure 6).

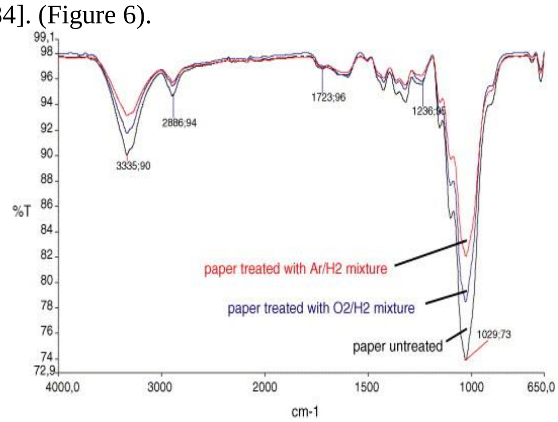

Fig. 6. Normalized ATR-FTIR spectrum spectra of ancient paper [84].

5.2.4. Plasma Jet System

A plasma jet system can generate a uniform glow discharge at one-atmosphere pressure using special gases and high-frequency power (Figure 7. a, b). The plasma can be sustained in gases like helium, air, or helium with a small addition of molecular gases like oxygen, nitrogen, hydrogen, or carbon tetrafluoride. Approximately 1% of the added gas molecules dissociate into radicals and atoms, which helps in effectively cleaning the surface of objects. An atmospheric pressure plasma jet (APPJ) configuration consists of an inner electrode powered by radio frequency, an outer electrode grounded, and gaseous plasma flowing between the electrodes and rapidly exiting. A plasma beam is emitted from a grounded external electrode [5]. Plasma jets operating in the air require higher power inputs and cooling gas flow rates compared to rare gases but can activate complex three-dimensional objects like wood [75,85]. However, most plasma jet systems have a limited treatment area of just a few square millimeters due to the small size of the exhaust stream [86].

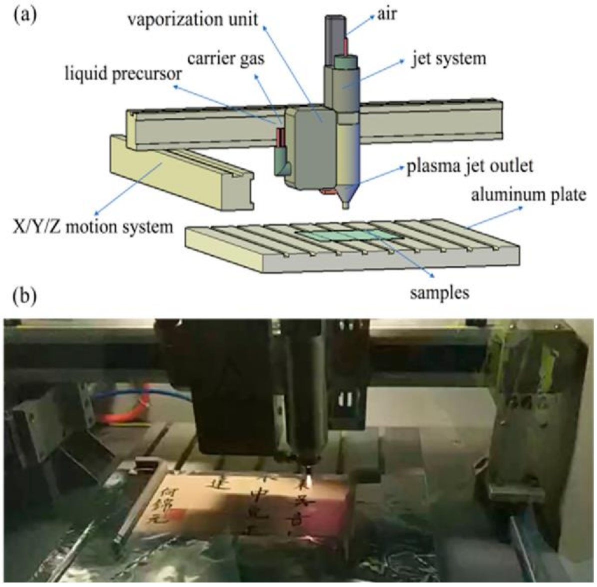

Fig. 7. illustrates the atmospheric pressure plasma system in a schematic diagram (a) and during atmospheric pressure plasma treatment (b) [5].

The epoxy coating on the sample surface is approximately 50 µm thick. After undergoing ageing procedures, the surface exhibits a slightly yellow hue due to the cross-linking process and the formation of C=C bonds. The surface texture is not as smooth as before, with a water droplet-like structure from the spray-deposited coating. After 25 minutes of cleaning, the coating is completely removed below the plasma jet point, leaving the surface undamaged. Analysis of the FTIR–ATR spectrum reveals that initially, the out-of-plane C–H curvature of the aromatic ring is suppressed, followed by the breaking of bridges between the epoxy chains composed of harder molecules. Eventually, the fragments are oxidized, producing H_2O, CO_2, and nitrogen monoxide (NO_x) [86].

5.2.5. Plasma Pen

The plasma pen is equipped with a piezoelectric direct discharge plasma system (Figure 8). It generates non-thermal plasma on the high-voltage side of a piezoelectric transformer (PT), making it suitable for compact and efficient devices that do not require a separate high-voltage supply. This technology uses a durable PZT ceramic piezoelectric component (Pb Zr Ti) to achieve highly efficient plasma generation at cold atmospheric pressure. The PT combines voltage conversion and plasma generation into a single component and is housed in a PTFE (Teflon) tube. The output side of the transformer features a monolithic active area of 16.8 mm2, while the input side has a multi-layer structure with copper electrodes [26,87]. The transformer's output temperature remains below 50 °C, allowing for the treatment of heat-sensitive components with plasma. The supply voltage is approximately 12V/2A, the output voltage can reach 20kV, the maximum input power is 10W, the operating frequency is around 50kHz, and the discharge temperature is kept below 50°C [39].

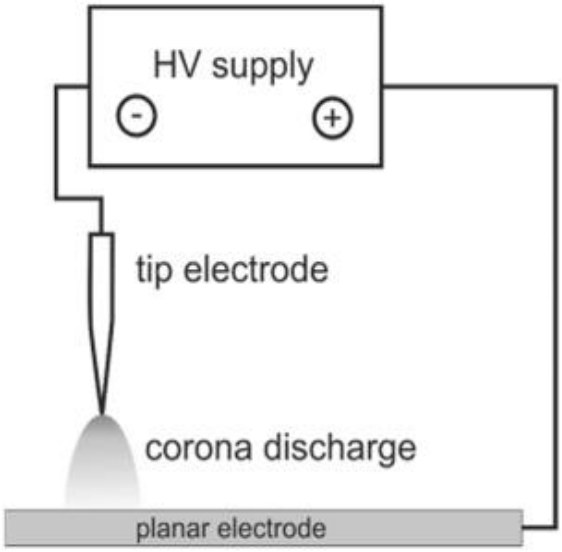

Fig. 8. Schematics of the general configuration of the corona ADRE plasma system [26].

6. Proposed Plasma Cleaning for Paper-Based Works

Cleaning is a crucial aspect of preserving heritage sites, especially when it comes to historical works like fine arts. Traditional cleaning methods can sometimes compromise the authenticity of these works, prompting specialists to explore new approaches. Cold plasma has emerged as a promising, non-destructive, and environmentally friendly technique for cleaning [26].

Surface cleaning involves several steps, including generating cleaning agents, transporting them to the surface, reacting with contaminants, and removing impurities. To ensure optimal efficiency, each step must be carefully analyzed. Various methods, such as atmospheric pressure treatment and vacuum processing, are used for surface cleaning.

Plasma technology creates a low-temperature environment that drives chemical reactions using electrical energy instead of heat. Unlike wet chemicals, plasma eliminates liquid waste and costly disposal requirements. Additionally, plasma treatment is a straightforward process that requires minimal supervision [57].

Plasma treatment can selectively modify the outer surface layer of objects on a nano-scale level [88]. enhancing labor productivity in preservation operations like cleaning, stabilization, and sterilization. Oxy-argon plasma is particularly effective for decontaminating objects with organic components, such as photographs [21,35].

Papers are a crucial source of information on cultural heritage, and plasma technology shows promise in the field of conservation. By treating paper with plasma, it is possible to remove bacterial contaminants in a single step and enhance the paper's durability [23]. Plasma treatment of naturally aged paper can increase its stability by around 20%. The bactericidal effects of plasma cleaning in an oxygen/hydrogen environment have been proven [89]. Coating plasma-activated papers with chitosan using DBD plasma further improves stabilization and durability [90].

Pflugfelder et al. [80] found that DBD jets are more appropriate for cleaning temperature-sensitive materials like historical books and documents, which can be challenging to preserve. Ioanid et al. [35] showed that old photographs can be improved in appearance through a cleaning process involving chemical or physical etching, without causing significant alterations to the plasma-cleaned surface.

Plasma cleaning techniques involve using discharge ingredients like radicals, ions, electrons, and photons to interact with stains on surfaces [91,92]. This process does not change the properties of materials and operates at a near-ambient temperature, making it safe for heat-sensitive materials. By adjusting conditions and process gases, plasma cleaning can effectively clean and modify surfaces, even on complex materials. It selectively alters surface roughness on a nanometric scale, making it suitable for conservation and restoration of historical objects in cultural material protection applications under low pressure and atmospheric conditions [21,93].

Plasma-based methods have shown promise in preserving cultural heritage artifacts. These methods involve treating the artifacts with different gases to clean their surfaces effectively. Gas mixtures, like argon and oxygen, are used in varying concentrations to remove different types of stains. The success of this cleaning process depends on the gas concentration and the nature of the stain [91-94].

The efficiency of plasma cleaning depends on the interaction between the paper surface and plasma, which is influenced by parameters like:

Factors that can affect the efficiency of plasma cleaning on paper surfaces include:

- The type of gas being ionized.
- The pressure and flow rate of the gas.
- The intensity and frequency of the energy used to excite the plasma.
- The duration of the cleaning process.
- The material of the paper surface.
- The distance between the plasma device (e.g., plasma beam) and the paper surface.

7. Advantages and disadvantages of using plasma cleaning techniques

Plasma treatment offers numerous benefits for historical objects, such as its unique properties and versatility in conservation and preservation of paper-based artworks. However, there are also some drawbacks to consider.

7.1. Advantages of Plasma Cleaning

In recent years, many research groups have focused on using plasma to protect cultural heritage materials and objects. Plasma cleaning offers several advantages in the preservation of heritage objects. For example, low-pressure plasma can effectively remove stains from paper using hydrogen plasma radio frequency. Oxygen-argon plasma is also useful for decontaminating organic objects such as photographs and papers [35,69]. The main advantages of plasma cleaning include its safety, environmentally friendly nature (green conservation), and its ability to work with temperature-sensitive materials without degrading them, thus preserving their properties. Plasma can be used at room temperature, preventing shrinkage or deterioration of organic artifacts. It allows for the cleaning of highly sensitive exhibits without leaving harmful residues. Additionally, plasma cleaning preserves the bulk material properties without causing material loss, as the reaction is selective and limited to the surface. This allows for precise timing to prevent deterioration. Plasma cleaning also enables the development of new devices with unique surface properties suitable for objects of all sizes [95,96].

A non-contact technique for removing organic deposits from surfaces is available. This method is suitable for restoring historical objects that are fragile and damaged due to age or other factors. The dry nature of the process eliminates the risk of leaching or swelling. It can combine various effects such as cleaning, disinfection, and consolidation of degraded artifacts by depositing superficial layers. These procedures achieve multiple operations like disinfection [97-99]. sterilization, and stabilization of objects in one device and application process. This makes chemical plasma processes suitable for conservation and preservation. Introducing plasma techniques can enhance productivity for individual conservation tasks like cleaning, stabilization, and disinfection. Plasma can treat objects made of different materials, including composite materials. Portable plasma reactors have been developed to process objects in museums or excavation sites. Processes can be easily controlled using DC, RF, or microwave power, gas, time, type, and pressure [100]. At the nanoscale, plasma ablation is selective and controllable.

7.2. Disadvantages of Plasma Cleaning

Plasma cleaning has some drawbacks that need to be considered. Continuous use of high power can lead to object degradation from extreme temperatures or uneven thermal stress [101]. Plasma reactors/cleaners are electrical devices that can pose a risk of electric shocks if safety precautions are not followed.

The effects of radiofrequency electromagnetic fields and radiofrequency plasma treatment on printing paper have been studied. Plasma treatments can alter the microstructures of papers, with exposure to radiofrequency magnetic fields reducing the material's degree of crystallization [102].

Plasma cleaning techniques have limitations due to technological constraints. Vacuum chamber size restricts the size of objects that can be cleaned, requiring the entire surface to be treated. The process can be costly and may not be easily monitored by on-site conservators [103-106]. Cold plasma cleaning, which uses low-pressure interactive plasma, necessitates complex vacuum equipment and can potentially damage objects if high power is used continuously, leading to heat-related damage. In addition, not only can the cellulose surface be altered during plasma treatment, but overall properties, such as tensile strength, can also be negatively affected by UV radiation under plasma conditions [23,107].

8. Methods for assessing the efficiency of stain removal using plasma cleaning

Assessing the efficiency of plasma stain removal can be done using different methods. There are some methods which include visual assessment, which includes examine of the stained surface before and after cleaning in order to detect the level of stain removal. Change of color measurement using UV. Spectrophotometer is considered one of the most common and effective technique that is used to measure the effectiveness of the cleaning process. It also provides quantitative data on the effectiveness of the plasma treatment. The investigation of the surface morphology using scanning electron microscope with big magnification is considered one of the most important techniques that allows for detailed examination of the surface morphology and structure before and after plasma treatment, providing insights into the physical changes induced by the treatment. Analysis using Fourier transform infrared spectroscopy (FTIR) provides an indication of the chemical composition changes in the paper before and after cleaning treatment. X-ray fluorescence analysis is crucial in the removal of stains using plasma cleaning as it helps identify the elemental composition of the stains before and after cleaning. This information is essential for determining the most effective plasma cleaning parameters and ensuring thorough removal of the stains. X-ray diffraction helps identify changes in the crystal structure of the stained material after cleaning. Contact angle measurement determines the surface wettability, indicating how well the stain has been removed. pH measurement monitors the acidity or alkalinity of the surface, which can affect the cleaning efficiency. These techniques provide valuable insights into the cleaning process and help ensure thorough removal of stains using plasma cleaning [16,19,108-112].

9. Conclusions

This study discussed how manuscripts, documents, and paper artworks are exposed to various forms of damage, which can be attributed to different internal or external factors. The study also shows that stains from various sources pose a significant problem for paper artworks. Additionally, the study highlights the various drawbacks of traditional cleaning methods, as mechanical cleaning can affect fragile and brittle paper artworks, and wet and chemical cleaning can lead to defects, including affecting inks, pigments, and dyes found on the paper materials. The article provides an overview of surface cleaning using atmospheric pressure plasma and vacuum. There are two types of plasma: thermal plasma and cold plasma. Cold plasma is better suited for the cleaning process of heritage materials. Cold plasmas are ideal for cleaning historical papers as they maintain room temperature. The energy is focused on ionizing the gas rather than heating it. There are several plasma cleaning methods, such as decontamination/sterilization, plasma surface activation, ablation, crosslinking, coating deposition, etc. The study showed that there are different sources such as radio frequency (RF), microwave frequency (MW), and acoustic frequency (AF). There are also some sources for low-pressure (vacuum) such as rf plasma and atmospheric-pressure plasma, which include atmospheric pressure glow discharge (APGD), dielectric barrier discharge (DBD) plasma, atmospheric discharge with runaway electrons (adre) plasma, plasma jet system, and plasma pen. the advantages and disadvantages of cleaning using plasma were also discussed. There are many methods of examination and analysis that can be used to evaluate the efficiency of plasma cleaning, including but not limited to infrared spectroscopy analysis, various microscopy techniques, color change measurement, pH value measurement, X-ray diffraction, and X-ray fluorescence, etc.

10. References

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