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Cleaning iron rust compounds from cotton textiles: application to Qing Dynasty armor

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Abstract

A composite structure consisting of cotton fabric and iron sheet was widely used in Qing Dynasty armor. Due to iron sheet corroding easily, the surfaces of cotton fabric were covered with numerous rust compounds, which has a significant negative impact on the relics. In this paper, by taking Qing Dynasty armor relics as the research object, the cleaning process was reported for cotton fabrics stained with corrosion products. Using an orthogonal experiment, rust stained model samples were used to explore a specialized and efficient cleaning process. Results show that the cleaning reagents, including ascorbic acid (mass fraction 10.0 g/L), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, mass fraction 10.0 g/L), and the surfactant composed of 70% rhamnolipid and 30% alkyl glycoside (mass fraction 8.0 g/L), could fully exert a synergistic effect. After treatment, the color difference (ΔE) value between the cleaned sample and the unstained sample is only 3.81. A series of comprehensive experimental results demonstrate that the cleaning procedure is effective and safe. There are almost no rust compounds and cleaning reagent residues, and no damage to cotton fiber. The reported wet cleaning process, aided by soft bristle brush, achieved good cleaning results, indicating that the process can be used to clean rust stain pollutants in Qing dynasty cotton armor.

Keywords Qing Dynasty armor, Cotton textiles, Cotton relics, Iron rust compounds, Wet cleaning method, Safety evaluation

Introduction

As a kind of protective equipment from the cold weapons age, the armor of the Qing Dynasty is one of the most intricate and delicate crafts in ancient China [1]. The protective studies on Qing Dynasty armor artifacts will contribute to investigating ancient Chinese military technology.

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In Chinese, "甲胄" means armor, and "胄" refers to the helmet. The helmet is the most exquisite part of the armor system, which symbolizes the status and social identity of the wearer. The fundamental part of the Qing Dynasty helmet is an iron half-shell, which is connected with protective gears for ear and neck (see Fig. 1). As shown in Fig. 1a, to meet the requirements of cavalry maneuvering, applying the traditional Han Chinese sustaining technologies, the structure of the Qing Dynasty armor is divided into outer and inner layers [2]. The outer layer is cotton fabric, the inner layer is composed of iron sheets, with two layers are fixed together by bubble nails. As shown in Figs. 1b, c, due to the severe corrosion from the iron sheets, the cotton fabric is heavily stained by iron rust compounds. Therefore, in order to preserve the ornamental value of armor relics, it is essential to eliminate rust compounds.

Iron is a reactive metal that corrodes electrochemically in the presence of water and oxygen [3, 4]. Biasini

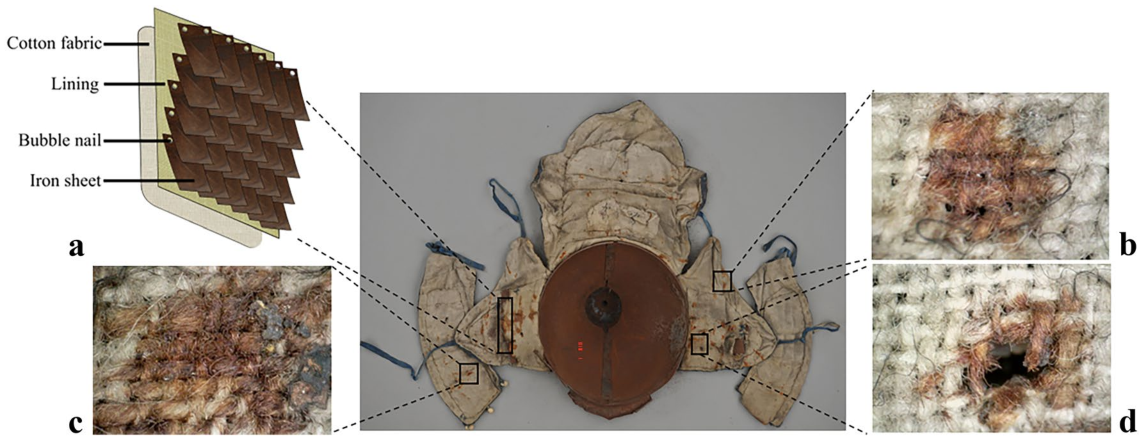


Fig. 1 Images of Qing Dynasty armor: **a** Armor structure diagram; **b** Micrograph of rust corrosion; **c** Micrograph of corrosion encrustation; **d** Micrograph of eroded yarn

V found that the corrosion process was still fairly active in the armor relics from sixteenth century [5]. The predominant component in the rust compounds from armor were goethite (α-FeOOH), lepidocrocite (γ-FeOOH), akageneite (β-FeOOH), magnetite (Fe_3O_4) and haematite (Fe_2O_3) [6, 7]. Among them, the γ-FeOOH structure is loose and unable to form a dense protective layer, consequently, water and oxygen can easily permeate and result in relics corroded. More importantly, in Fig. 1d, it can be seen that the fibers are more likely to break in the areas stained by rust compounds. It is not only due to the abrasion of iron rust but also to the fiber's acid hydrolysis the accelerated by metal ions [8, 9]. Hence, the removal of rust compounds is crucial for the preservation of armor relics.

There are numerous ways of removing rust corrosion products, such as mechanical [10], chemical [11], and laser methods [12, 13]. Physical and laser methods are safe and effective for removing rust compounds on the surface. However, it is poor effective in removing rust compounds embedded in the fabric. By microscopic observation, it was determined that the iron rust had permeated deeply into the textile structure and that the yarns were wholly coated by iron rust (see Fig. 1b). Therefore, together with removing of surface iron corrosion encrustations with a soft bristle brush, the rust compounds embedded in the fabric need to be cleaned using chemical wet cleaning.

Generally, a surfactant will play roles in three aspects: promoting textile wetting, dislodging and separating stains from fibers, and forming micelles to dissolve insoluble substances such as fat and other stains [14]. Furthermore, the mixed use of surfactants can enhance solubilization [15, 16]. In academic studies on the protection of iron relics, EDTA-2Na was found to form a stable complex with iron ions, playing an oxidation-removal effect [17]. In addition, ascorbic acid as a vitamin can reduce insoluble Fe (III) to soluble Fe (II) and form a water-soluble chelate with iron [18, 19]. However, the above single reagent has a limited cleaning effect on rust-stained cotton relics. In order to improve the cleaning effect of rust compounds, the surfactant, EDTA-2Na and ascorbic acid were combined together in this paper. As shown in Fig. 2, ascorbic acid initially reduces insoluble Fe (III) to soluble Fe (II), increasing the solubility of rust compounds [20, 21]. Meanwhile, the nonionic surfactant alkyl glucoside decreases the surface tension between rust compounds and fabric, whereas the anionic surfactant rhamnolipid accelerates the transfer of Fe (II) into the solution [14]. Finally, by complexing with iron ions, EDTA-2Na reduces the Fe (II) concentration in a solution system, thereby maintaining the surface activity of the surfactant, and accelerating the reaction.

In this paper, the cleaning reagents and their conditions were explored for rust-stained samples. Based on a comprehensive evaluation of the cleaning effect and safety of the stained model samples, Qing Dynasty armor relics were cleaned, and their cleaning effectiveness and safety were evaluated.

Experiment

Experimental materials

Fabric: Plain weave cotton fabric (120 g/m^2).

The reagents, including ascorbic acid ($C_6H_8O_6$), ethylenediaminetetraacetic acid disodium salt ($C_{10}H_{14}N_2Na_2O_8$, EDTA-2Na), sodium citrate ($C_6H_5Na_3O_7$), rhamnolipid (90%), and alkyl polyglucoside ($C_{16}H_{32}O_6$, APG10), were

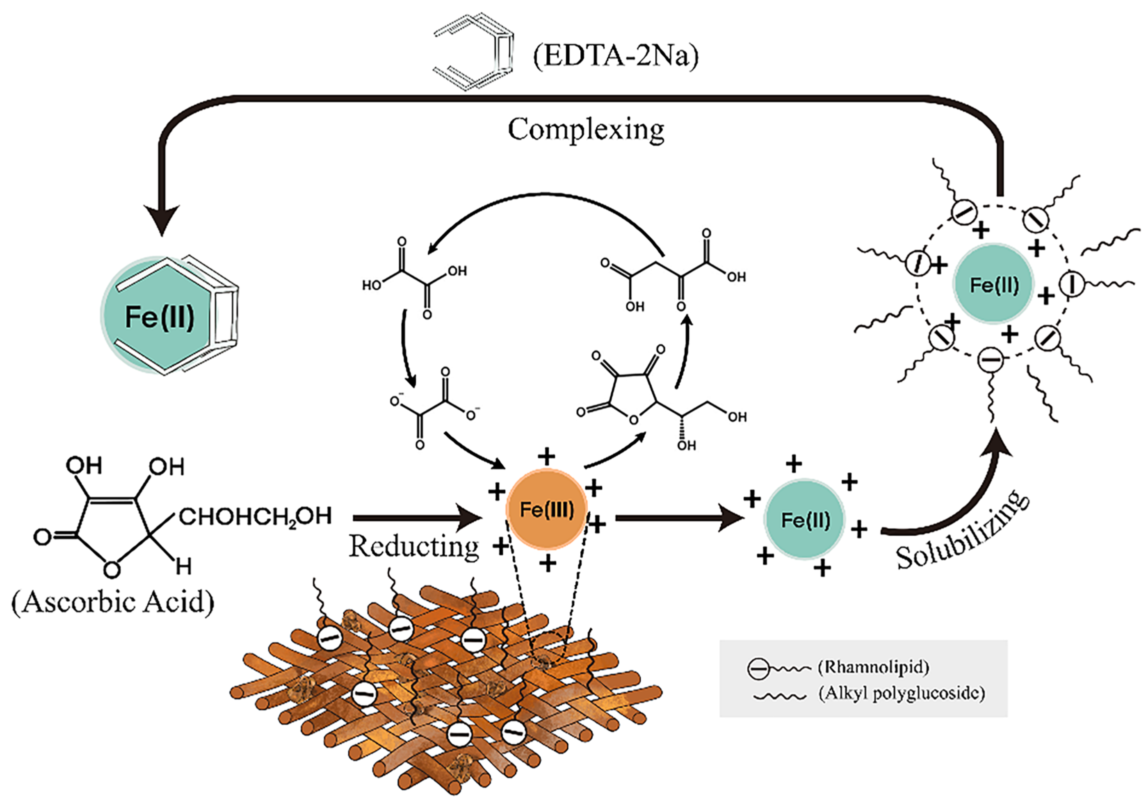


Fig. 2 Schematic diagram of cleaning principle

used in the cleaning experiment, which were purchased from Sigma (Sigma–Aldrich, Mo, St. Louis, USA) and with the level of AR grade.

The armor is from early Qing Dynasty collected from National Museum of China.

Experimental methods

Model sample preparation

To prepare substitute samples for relics, after the iron block rusted at the temperature of 25 ± 2 ℃ and humidity of 65 ± 5% for 6 months, the cotton fabrics (after pretreatment) were tightly attached to the surface of the corroded iron block. A solution (pH 6–7) with 2% NaCl was sprayed every 12 h to accelerate rusting of the iron block and transfer to the fabric. To keep the sample stained uniformly, it is necessary to ensure the fabric is flat. After ten days, the cotton fabric was taken off and then aged for 100 h by hygrothermal aging, under an temperature of 120 ± 2 °C and a humidity of RH 80 ± 5% [22]. The value of the color difference(ΔE) between the rust compounds stained model sample and the unstained sample was 60.60.

Research on the cleaning procedures

Cleaning process Since textile relics are fragile and have aged for a long time, the cleaning conditions should be designed mildly. Considering the cleaning effect and the aging degree of Qing armors, the cleaning operation was controlled at a relatively mild temperature of 40 ℃, cleaning for 30 min, pH value of 5, and bath ratio of 1:100. The cleaning processes were as follows: At first, the ascorbic acid, EDTA-2Na, and surfactant (rhamnolipid/alkyl polyglucoside, 70/30) were dissolved in deionized water in turns. Secondly, sodium citrate was added to adjust the pH value. Finally, the rust compounds stained model samples were put into the cleaning solution and heated in a water bath for 30 min. After treatment, the samples were cleaned and soaked in deionized water until the solution was neutral, then dried naturally.

Cleaning experiment by orthogonal arrangement According to the previous experimental results, based on model samples, an orthogonal array [$L9(3^4)$ matrix] was utilized to design the experiment. Optimal conditions were obtained by the results of the orthogonal experiment and data analysis [23]. Then, the range and variance analyses were carried out to learn the roles of each factor. Finally, the experiment was repeated under optimal conditions to verify the results.

Cleaning effect and safety evaluation

(1) Colorimetric measurements
Colorimetric analysis of samples was performed by colorimeter (Colori7, X-rite, USA).
Each sample was tested nine times. The color difference(ΔE) values before and after cleaning were calculated by the CIEDE2000 color difference formula. Under the premise of keeping the background color unchanged, according to the colorimetric data or the colors changed in the experiment, the cleaning effect was evaluated.

(2) Morphological observation
Morphological observation of fabrics was performed by a microscope (XSP-8CA, Shanghai Optical Instrument Factory, China). Microscopic examination of fibers was carried out by Field Emission SEM (JSM-6360LV, JEOL Ltd., Japan).

(3) X-ray photoelectron spectroscopy (XPS)
The examination of XPS was performed by an X-ray photoelectron spectrometer (Nexsa-G2, Thermo Fisher Scientific, USA), at the emission current of 5 mA and voltage of 10 kV. X-ray source type is monochromated Al K-Alpha, and X-ray spot size 400 µm. The scanning range of the binding energy is 0–1 200 eV, the pass energy is 100 eV, and the step is 1 eV when scanning with a wide spectrum. The scanning range of the binding energy is 700–740 eV, the pass energy is 30 eV, and the step is 0.1 eV when scanning with high resolution scans.

(4) Spectroscopic analysis
Attenuated total reflection Fourier transform infrared spectroscopy(ATR-FTIR) is a non-destructive test, which can characterize the degree of deterioration of relics from the molecular level [24, 25]. The spectrum of samples were acquired by a Fourier Transform Infrared Spectrometer (iS10, Thermo Scientific Inc., USA), equipped with an Attenuated Total Reflectance (ATR) diamond cell for scanning in the 4000–400 cm^{-1} region, at a resolution of 8 cm^{-1}. The infrared spectra of cotton relics were characterized to obtain their structural information [26, 27].

(5) Fabric tensile properties testing
The changes in tensile mechanical properties can characterize the damage by cleaning treatment. In order to ensure the objectivity of the evaluation results, the unstained samples were treated at the same conditions of damp and heat aging as those of the rust compounds stained model samples. In accordance with the test method GB/T 3923.1-2013, the tensile properties of samples before and after cleaning were tested by a universal material testing machine (3367, Instron, USA). Samples were cut into 200 mm × 50 mm, with the stretch along the length. The stretching speed was 100 mm/min, and the pretension was 2N. After testing, the average values were calculated, with five repeats for each sample.

Results and discussion

Orthogonal experiment

Thanks to the previous screening results of surfactants, the active cleaning effect was exhibited at a ratio of 0.7 rhamnolipid: 0.3 alkyl glycoside (APG10). According to the results of single-factor experiments, the experiment was based on an orthogonal array [L9 (3^4) matrix], where the following three variables were analyzed: ascorbic acid dosage (factor A), EDTA-2Na dosage (factor B), and surfactant dosage (factor C) (see Table1). The color difference values(ΔE) of the model samples before and after cleaning were served as the evaluation indices.

Table 1 Arrangement and results of the orthogonal cleaning experiment

Factor	A. Ascorbic acid (g/L)	B. EDTA-2Na (g/L)	C. Surfactant (g/L)	Δ*E*
Level				
1	9.0	7.0	7.0	
2	10.0	8.5	8.0	
3	11.0	10.0	9.0	
Trial No.				
1	1	1	1	46.61
2	1	2	2	52.96
3	1	3	3	53.81
4	2	1	2	48.92
5	2	2	3	54.03
6	2	3	1	55.46
7	3	1	3	48.36
8	3	2	1	54.36
9	3	3	2	56.19
K_1	51.13	47.96	52.14	
K_2	52.80	53.78	52.69	
K_3	52.97	55.15	52.07	
R	1.84	7.19	0.62	

K is the average value of each factor level, and R is the ranges of K

Table 2 Analysis of variance of the orthogonal cleaning experiment

Variance source	SS	DOF	F value	P value
Factor A	6.24	2	346.50	< 0.01
Factor B	87.45	2	4858.06	< 0.01
Factor C	0.69	2	38.50	0.01 < P< 0.05
Error	0.02	2		

SS stands for sum of squares, DOF stands for degree of freedom, and P value represents significance

According to the L9 (3^4) matrix, nine experiments were carried out, and the results are shown in Table 1. It shows that the range of the color difference (△E value) of the samples varies from 46.61 to 56.19. It can be seen from Table 2 that the F values of three factors are sorted as follows, EDTA-2Na > ascorbic acid > surfactant (B > A > C), which shows that the great significance (P < 0.01) belongs to EDTA-2Na and ascorbic acid, and the surfactant have significant effects on the cleaning results (0.01 < P< 0.05). The optimal level of reagents was $A_2B_3C_2$, (mass fraction of ascorbic acid 10.0 g/L, EDTA-2Na 10.0 g/L, and surfactant 8.0 g/L). Three verification experiments were carried out to confirm that the optimal experimental conditions determined by the orthogonal experiment were reliable. The color difference (ΔE) was 56.79 ± 0.48, similar to the orthogonal experiment results. After cleaning, the color difference between the cleaned sample and the unstained sample was only 3.81, indicating that most rust compounds were removed.

Cleaning effectiveness and safety evaluation

To ensure the feasibility and safety of the cleaning process in armor relics, the cleaning effect and safety of the model samples were evaluated by morphology observation, photoelectron spectroscopy, chromaticity value test, and tensile property test.

Morphology observation

The microscope images of the model samples before and after cleaning are shown in Fig. 3. Before cleaning, the surface of fabric was covered with rust compounds, showing a brown–red color and a vague fabric structure. After treatment, the rust compounds in the fabric were primarily eliminated. No damage was discovered, and the organizational structure of the sample was intact.

Scanning electron microscopy (SEM) was utilized to compare the longitudinal morphology of the cotton fibers before and after cleaning, so as to analyze the impact of the cleaning procedure on the cotton fibers. Before treating, the surface of cotton fibers was covered with a thick layer of rust compounds (see Fig. 3a, b), making it impossible to see surface details. After the cleaning process finished, the natural texture in the fiber was fully exposed, and the fiber's appearance was restored without residuals of rust compounds almost (see Fig. 3c, d). In addition, no fiber cracks, splits, breaks, or other damages were discovered.

X-ray photoelectron spectroscopy elemental analysis

XPS analysis was performed on the cotton fabric surface before and after cleaning to verify the cleaning effect.

The surface of model samples before and after cleaning was demonstrated by XPS (see Fig. 4). As displayed in Fig. 4a, the peaks at 532.1, 712.1 eV are associated with the O atoms and Fe atoms, respectively [28], which observably decreased. This indicates a high efficiency of removing iron rust compounds. Figure 4b shows a high-resolution scanning comparison of the Fe (2p), showing the changes in content of iron elements on the surface of cotton fabric. As Fig. 4b shows, compared with the model sample before cleaning, after cleaning it has no discernible absorption peak, proving that the rust compounds have been eliminated. Furthermore, there is no satellite

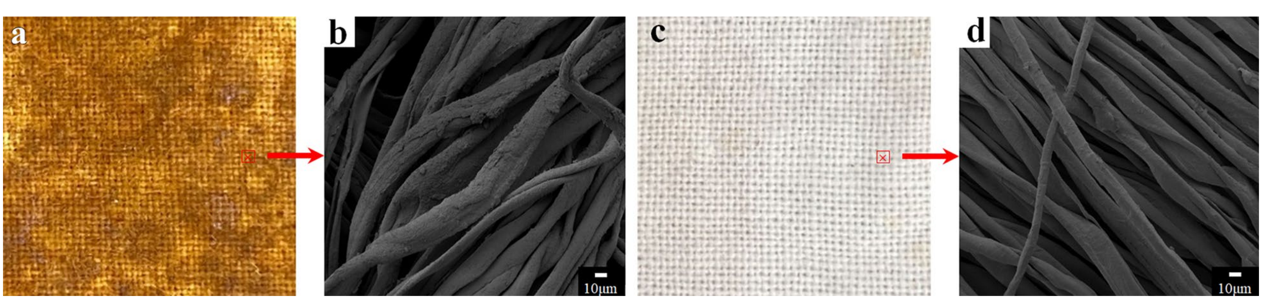
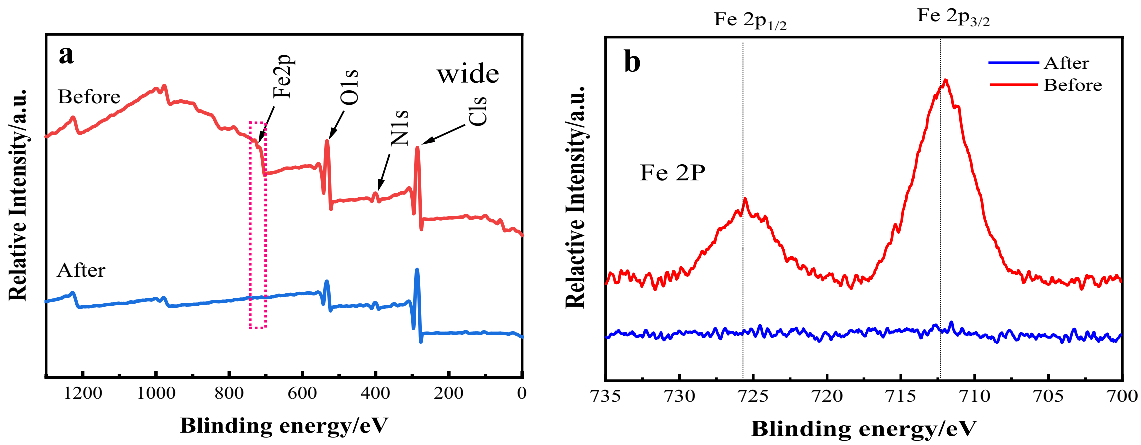


Fig. 3 Leftward, image of the model sample before cleaning **a** Microscope image (5 ×). **b** SEM image (500 ×); Rightward, model sample after cleaning. **c** Microscope image (5 ×). **d** SEM image (500 ×)



Notes: before cleaning (red line); after cleaning (blue line).

Fig. 4 XPS spectra of rust compoundson cotton fabrics before and after cleaning. **a** Wide spectrum. **b** Fe(2p) spectrum. Before cleaning (red line); after cleaning (blueline)

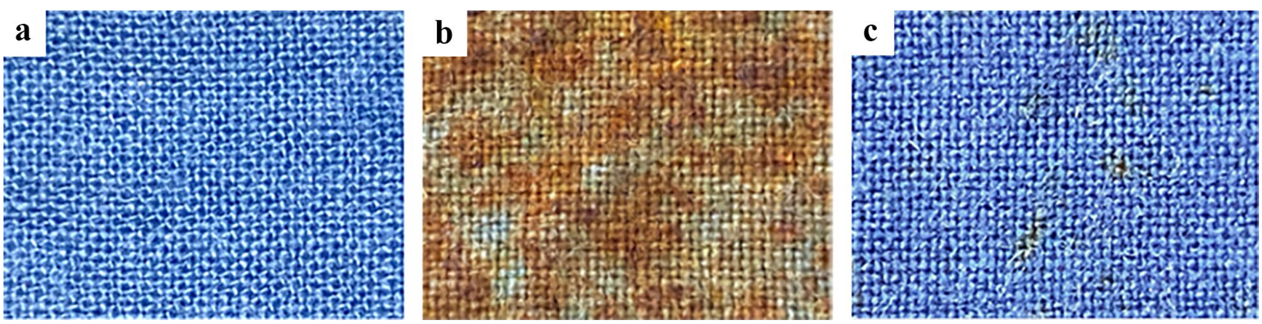


Fig. 5 Microscope images of the indigo-dyed sample **a** unstained sample. **b** Stained sample before cleaning. **c** stained sample after cleaning. Magnification used: 5×

peak at 718 eV (red line) in the high-resolution spectrum of the model sample before cleaning [29], indicating that the main component of the rust compounds is Fe (III).

Influence on the fabric color

The color of Qing armor varied greatly due to differences in arms, combat targets, and environment. Given its durability and dirt resistance, indigo was the most widely used color in Qing armor. To avoid the interference of color changes on the assessment of cleaning effectiveness, a cotton fabric sample with natural color was first cleaned in this study. Next, to ensure the cleaning process is suitable for colored armored relics, indigo-dyed cotton fabric stained with rust compounds was cleaned so that the influence on indigo color was analyzed.

Table 3 Chromaticity value of indigo-dyed sample before and after cleaning

Sample	L value	a value	b value	ΔE value
Unstained sample	30.94	0.49	− 20.75	–
Stained sample before cleaning	38.73	8.84	23.77	45.96
Stained sample after cleaning	30.66	− 0.14	− 19.93	1.07

As shown in Fig. 5 and Table 3, the indigo color on the stained sample was covered with rust compounds before cleaning and the overall color was reddish-brown (see value a and value b in Table 3). After cleaning, the color sense and luster of the fabric were resumed and the color difference (value ΔE) against the unstained sample was only 1.07, indicating that the cleaning process

Table 4 Effect of the cleaning process on tensile properties of cotton fabrics

Sample	Condition	Breaking elongation, /%	Breaking strength, /N·5.0 cm^{-1}	Breaking work, /J
Unstained sample	Soaked in deionized water	15.09 ± 0.51	292.72 ± 21.08	2.32 ± 0.23
	Treated by cleaning solution	14.43± 0.59	290.80 ± 37.20	2.23 ± 0.42
Stained sample	Soaked in deionized water	8.77 ± 0.69	58.86 ± 14.26	0.31 ± 0.09
	Treated by cleaning solution	10.32 ± 0.63	117.71 ± 9.57	0.73 ± 0.07

had no impact on the indigo color. This is because the indigo dye is insoluble in water, making it difficult to fade on the fiber. Even though the indigo is reduced to leuco vat acid (II) in an acidic aqueous solution, its solubility is extremely low, and it is equally difficult to fade [30, 31]. As a result, the cleaning process has no impact on the indigo color and can be used to remove rust compounds from the fabric dyed with indigo.

Tensile test

The results of tensile properties are shown in Table 4. There is no significant difference between the cleaning solution and deionized water treatment in the tensile properties of the unstained samples ($P > 0.05$), which show that the cleaning process did not damage the mechanical properties of cotton fabric. Compared with the deionized water treatment, the tensile properties of the stained samples treated with cleaning solution were significantly improved ($P < 0.01$). This is because that, after the rust compounds were removed, the friction resistance between fibers decreased, and the yarns moved easily, with more yarns bearing an external force in the same stress zone. In addition, compared with the unstained sample, the tensile properties of the stained model sample were significantly degraded, indicating that the harm caused by rust compounds to the cotton fabric cannot be disregarded.

To sum up, since rust compounds do great harm to textile relics in long-term storage, cleaning is crucially necessary. The cleaning process described in this paper removed rust compounds effectively, which are relatively mild and don't damage cotton fabric. Meanwhile, the indigo color was almost unaffected by the cleaning treatment. It can be applied in the cleaning of armor relics. Additionally, rust compounds cause significant harm to textiles, which demands a detailed study.

Cleaning of Qing Dynasty armor

After the effectiveness and safety of cleaning were confirmed, the process was used to clean the natural color and indigo fabrics of Qing dynasty armor relics separately. Then, the cleaning effect of the process on the rust compounds of relics and the impact on the indigo color of relics were gained.

Cleaning effect on the fabric of the relics

As shown in Fig. 6a, there is a certain difference in the rusts between the relics and the model samples. The fabric armor is stained by not only rust stains but also corrosion encrustation, the latter attached to fabric surface. It is shown that the rust corrosion products on relics are uneven in distribution, size, and degree. When designing the removal method, the condition of the rust corrosion products on relics should be taken into account. Hence, the wet cleaning process was used to treat the fabric armor, aided by soft bristle brush in this paper. Then observations under the microscope were also made.

The cleaning effect of the cotton fabric from Qing dynasty armor is shown in Fig. 6. For rust compounds, this cleaning process worked well. Although the corrosion encrustation was not removed completely by cleaning reagents, the rust particles became loose and small, and the combined force with the cotton fabric was reduced. It was removed easily with a soft bristle brush, which reduced the damages to the relics. For plant indigo-dyed fabric armor, an effective result was also achieved by adopting this cleaning process. After cleaning, the fabric structure became visible and the indigo color was clear.

In addition, the process also has a good cleaning effect on other stains in the fabric armor (As shown in the elliptic mark in Fig. 6c). This is because the surfactant and complexing agents have a good cleaning effect on general stains.

Spectroscopic analysis (ATR-FTIR)

The results of the infrared spectroscopic of armor relics are shown in Fig. 7.

As annotated in Fig. 7a, two test points were selected, where test point No.1 is stained by rust compounds and test point No. 2 is not. As shown in Fig. 7b, there are several significant infrared absorption bands in the infrared spectra of the test point No. 2. Band at

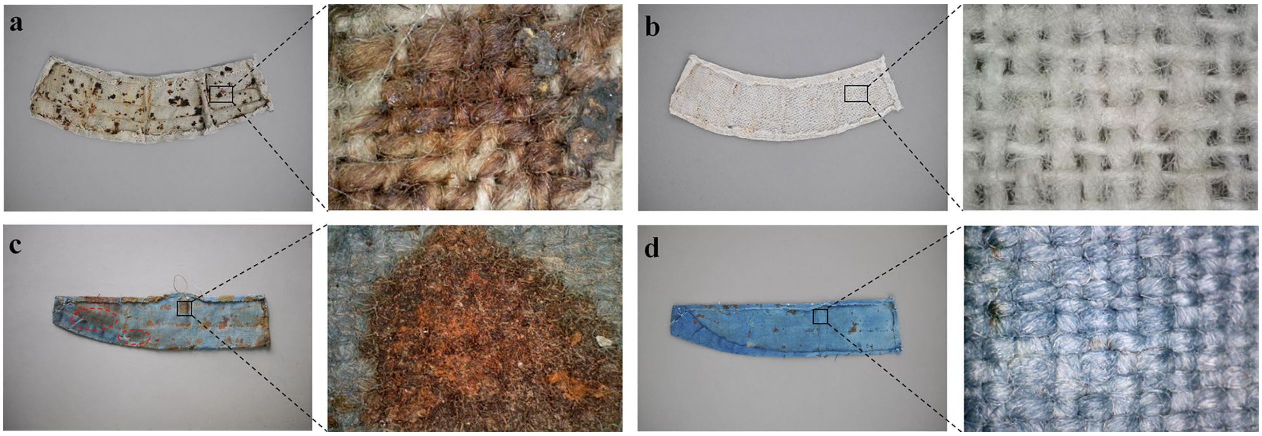


Fig. 6 Upper, comparison of natural color fabric armor: **a** before cleaning. **b** after cleaning; Lower, comparison of plant indigo-dyed fabric armor: **c** before cleaning. **d** after cleaning. Magnification used: 50 ×

around 3330–3340 cm^{-1} is characteristic of the stretching vibration of OH groups; band at 2890–2910 cm^{-1} is asymmetrical and symmetrical stretching of C-H groups and several peaks appear in the fingerprint region 1600–600 cm^{-1}. The infrared spectra of testing point No. 1 are pretty different before and after cleaning. Before cleaning, the characteristic bands of the sample were greatly weakened, owing to the blocking of the serious rust compounds. Compared with test point No. 2, the intensity of OH group's characteristic band at 3 336.9 cm^{-1} decreased after cleaning, while the intensity of the rest of the characteristic bands remained unchanged. This indicates that the number of hydroxyl groups in cotton cellulose was significantly reduced, presumably because the iron ions in the rust compounds were easily complex with the hydroxyl groups. Meanwhile, no aging peaks and no significant peak displacement were found. It shows that the cleaning process can effectively remove the rust compounds on the armor of the Qing Dynasty relics without damaging the fabric.

Conclusions

In this paper, the cleaning techniques of cotton fabric with rust compounds stained are studied and the techniques are applied to Qing dynasty armor. The following conclusions are drawn.

1. According to the results of the orthogonal experiment, the cotton fabrics with rust compounds were cleaned effectively under the conditions of ascorbic acid mass concentration of 10.0 g/L, EDTA-2Na mass concentration of 10.0 g/L, and surfactant mass concentration of 8.0 g/L. In the process, the importance of cleaning effect decreases in turn, from EDTA-2Na, ascorbic acid to surfactant.
2. Results of safety and effectiveness evaluation show that most of the rust compounds were removed by the cleaning treatment without damaging indigo color, fabric and fiber structure. It can be seen that after cleaning, the tensile properties of the stained samples are greatly restored. The elongation at break recovered from 8.77% to 10.32%, and the tensile break-

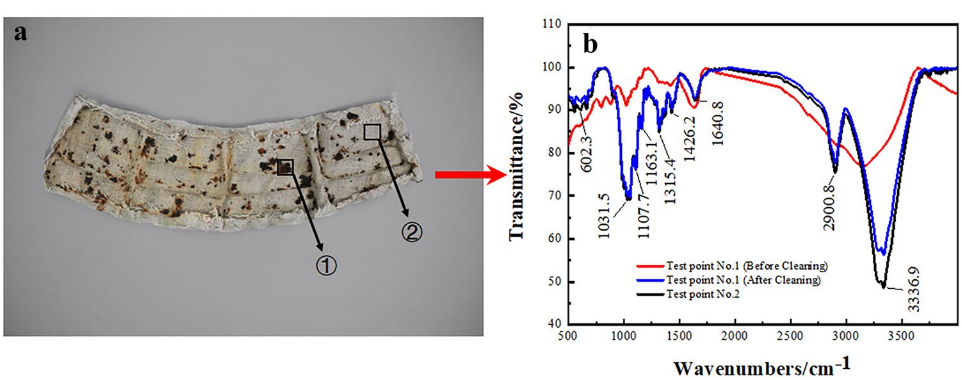


Fig. 7 Infrared spectrogram of the cotton fabric in armor of the Qing Dynasty

ing strength recovered from 58.86 N/5.0 cm to 117.71 N/5.0 cm. Therefore, the removal of rust compounds is of positive significance for the protection of armor relics.

3. For the rust compounds stained Qing dynasty armor, effective cleaning results were achieved by combining the chemical cleaning method and physical brushing. After cleaning, the fabric structure and indigo color are obvious, and the molecular structure of cotton cellulose remains intact.

Even though no adverse effects are found in this cleaning process, it should be used with caution on the mordant dyed fabrics, because of EDTA-2Na complexing with metal ions. In addition, the method of chemical wet cleaning would cause fiber swelling. For these reasons, some new cleaning methods will be explored to reduce the impact on fabric color and fiber swelling.

Abbreviations

EDTA-2Na	Ethylenediaminetetraacetic acid disodium salt
SEM	Scanning electron microscopy
XPS	X-ray photoelectron spectroscopy
ATR-FTIR	Attenuated total reflection Fourier transform infrared spectroscopy

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Author contributions
Conceptualization; YW. Funding acquisition; YW, HL, BM. Investigation; BM, PG, ZZ. Methodology; YW, BM. Writing-original draft; BM. Writing-review & editing; YW, HL, BM, ZZ, PG. All authors have read and approved the final manuscript.

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Availability of data and materials
All data generated or analyzed during this study are included in this manuscript.

Declarations

Competing interests
The authors declare that they have no competing interests.

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