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Chemical characterization and origin of dyes used in the manufacture of Beninese cultural heritage objects

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Abstract

Six objects of Beninese cultural heritage provided by African and Confluences museums of Lyon (France) were the focus of this study. The characterization of colored compounds was achieved using: microchemical tests, Fourier transform infrared spectroscopy and liquid chromatography coupled to a photodiode array detector. The main results reflect the presence of organic compounds like indigotin, 2-hydroxynaphthoquinone, and mineral ions such as Al^{3+} , S^{2-} , Na^+ , and Fe^{3+} . Dyes were identified from *Philenoptera cyanescens* (Yoruba indigo) and *Lawsonia inermis* L. (henna); pigments were identified as laundry blue, Prussian blue, and iron oxides. All of these data therefore make possible the conservation and the restoration of these objects while maintaining their visual and functional integrity.

KEYWORDS

chemical characterization, colored materials, conservation, cultural heritage objects, liquid chromatography, museum collections, restoration

1 | INTRODUCTION

The dyes used in the manufacturing of heritage works represent an important cultural element.¹ Indeed, in all parts of the world, natural dyes have been used since the earliest times until the end of the 19th century, when they were supplanted by the discovery and the economic development of synthetic dyes: sources of new dyes and pigments for painting.²

These organic colors in ancient materials were obtained from plants, insects, crustaceans, and lichens.³ Moreover, mineral substances came from the red or the yellow colored earths. Their mixture offers in particular a palette of colors very rich in hues and shades. In fact, the recurring problem concerning artistic works of African origin is the lack of documentation about the dyeing materials used,⁴ or its imprecision, in particular for objects collected in the past and today in a rather alteration state of aging or anthropic

degradation. The objects selected for this work reveal these shortcomings. However, according to some inscriptions and/or characteristics of representation, it has been specified that these objects were collected in the 1900s, and they are originate from the Yoruba-Nago region, the current territory of the Republic of Benin.

They belong to the collections of the African and Confluences Museums of Lyon (France). Their peculiarity beyond aesthetics is that they were all destined to a specific use in their locality of origin. Indeed, masks (Guèlèdè), figurines (Ibèji), Shango or hunter suits worn during specific rituals, especially during the hunt or other propitiatory ceremonies, amplify the spiritual vision of the wearer.

Ethnic objects remain characterized by the genius of their assembly, the expression, and the mixture of the materials. The objective of this work is to promote the restoration of these objects by providing data to determine the origin of the dyes/pigments and the likely period of their manufacture.

Indeed, the identification of the tinctorial constituents, whatever their aging/degradation, will permit to obtain indications about their plant, animal, or mineral source as well as their composition.

In view of this, an early ethnobotanical study was carried out with the aim of selecting and characterizing the coloring principles of the dye plants most used in South Benin for the manufacturing of artistic and artisanal objects, and of creating a data bank.^{5,6}

Each coloring material corresponds to a mixture of various organic compounds and/or mineral substances; moreover, any medium can be treated with several of them. It is therefore necessary to use specific analytical techniques for each type of material. After a preliminary study by microscopy, all the samples were analyzed by Fourier transform infrared spectroscopy (FT-IR),^{7,8} in order to characterize the organic and/or mineral nature of the dyestuffs present in the samples.

Concerning the coloring matter of mineral origin, each of the characteristic spectral bands was studied in order to characterize the nature of the pigment used. A complementary study was also carried out by microchemical tests.^{9,10} These tests allow the identification of the constituent ions of the mineral color.

Organic dyes were studied by high performance liquid chromatography coupled to a photodiode array detector (HPLC-PDA), a technique of choice for the separation and the identification of nonvolatile compounds such as organic coloring components.^{11,12}

The analysis of colored materials was carried out from the study of reference substances by determining the specific spectral and chromatographic fingerprints to deduce the composition of the main components.

The purpose of this article deals with the characterization of the coloring substances sampled from a few Beninese cultural heritage objects in order to provide useful information on their origin and thus to have a better knowledge of these collections and to organize their restoration and preservation.

2 | MATERIALS AND METHODS

2.1 | Sampling

The ethnic objects consisted of two “Guèlèdè” masks, a statuette of twins “Ibéji,” a monkey, a fetish, and a hunting vest, belonging to the collections of the African and Confluences museums of Lyon (France). Objects are described in Table 1. Samples were collected following the methodology for sampling from materials of cultural property (ie, European Committee for Standardization EN 16085:2011-12). Due to the destructive nature of sampling, they were carefully chosen from areas that had no aesthetic or iconographic value for future reconstruction.

2.2 | Fourier transformed infrared spectroscopy

The FT-IR spectrometer was a Thermo-Nicolet AVATAR 360 FT-IR in transmission mode with OMNIC 32 software. FT-IR spectra were collected in the 400-4000 cm^{-1} range recording 64 scans per spectrum. About 5 mg of each sample was mixed with 150 mg of KBr, homogenized, and pressed under 10 T cm^{-2} in order to form a thick KBr pellet. Samples were directly analyzed by infrared spectroscopy.

Only the sample referred S6 was analyzed by attenuated total reflectance (ATR) because of the presence of the textile.

2.3 | Microchemical tests

These chemical tests are useful for identifying mineral compounds. The analysis of salts can be carried out by microchemical tests on very small amounts of sample. Analysis consists in the qualitative detection of single ions in more or less concentrated salt solutions. The reaction products are visible with a microscope, and they correspond to the formation of a precipitate, a color change of the solution, or a change of physical state. The method has good sensitivity for mineral pigments and fillers, using predominantly acid-base, redox, and complexation chemical reactions. Solvents and reagents were purchased from Merck (Darmstadt, Germany).

Detection of Fe^{3+} and Fe^{2+} iron oxides was performed by adding a drop of concentrated HCl (37%) to the collected sample. Then, adding a drop of potassium ferrocyanide solution (100 g L^{-1} in water) gave a blue color in the presence of Fe^{3+} , while the addition of potassium thiocyanate solution (160 g L^{-1} in water) characterized the Fe^{2+} ions via a blood red color.⁹ In a first step, characterization of ferric ferrocyanide or Prussian blue was performed by the identification of the Fe^{3+} and Fe^{2+} ions.⁹ Then, adding a drop of 4N NaOH, the pigment was completely discolored and the formation of an orange-brown precipitate of iron hydroxide $\text{Fe}(\text{OH})_3$ was observed.¹³ The identification of blue laundry led to the search ions sulfide S^{2-} , aluminum Al^{3+} , and sodium Na^+ . The pigment was diluted in HCl (3 N) and azide iodine-sodium reagent was added. It occurred then a H_2S gas release in the presence of sulfide followed by discoloration of the solution.¹³ The addition of an acetate buffer solution to the pigment and then an aluminon III (aurintricarboxylic acid ammonium salt) solution revealed the presence of aluminum after a few minutes by a dark red or pink coloring observed.^{10,13} To detect Na^+ , an acetic acid solution (30%) was directly added on pigment particles deposited on a filter paper. After drying, it was covered with a drop of uranyl acetate zinc reagent and observed under UV light ($\lambda = 254 \text{ nm}$). The presence of sodium resulted in the emergence of a highly fluorescent spot.¹³ The analysis and observations were carried out with a binocular microscope and by testing a positive blank for each chemical reaction.

TABLE 1 Objects from Beninese cultural heritage

Reference	Object
S1 (dark blue) Guèlèdè mask African museum; ref 401.940.033
S2 (brown red) Monkey Confluence museum; ref. 60004085
S3 (blue) Ibéji twins African museum; ref 501.931.002
S4 (blue and red) Fetish Confluence museum; ref. 60003627

TABLE 1 (Continued)

Reference	Object
S5 (orange-red) Guèlèdè mask Confluence museum; ref. D979-3-0792
S6 (dark blue) Hunter costume jacket African museum; ref. 2013.0.152

2.4 | Chromatographic analysis

2.4.1 | Sample preparation

Sample preparation was performed in function to the nature of the pigment by using a nondenaturing decomplexation method.¹⁴ Indeed, 0.5-1.5 mg of dyestuff was treated with 500 μ L of acetate buffer solution (pH = 4.3) supplemented with 1.5 mL DMF-MeOH (1:1 vol/vol) and then sonicated (Solex prototype 180, R.E.U.S, France) during 10 minutes. The extract was filtered, evaporated to dryness, and then taken in 250 μ L of methanol before injection in HPLC. The blue textile sample S6 was directly extracted with 2 mL of DMF-MeOH (1:1 vol/vol).

2.4.2 | Analytical conditions

HPLC-PDA analysis was carried out using a Waters liquid chromatography system consisting of a high-pressure ternary pump (Waters 600), a vacuum degassing, an autosampler (20 μ L injection loop) and a PDA detection system (Waters 2996). The liquid chromatography apparatus was equipped with a Symmetry column Shield RP18-e (5 μ m, 4.6 $\times$ 250 mm) for the analysis of the collected red dyes dyestuffs and a core shell particles C18 column (Kinetex Core-Shell RP-18, Phenomenex 2.6 μ m; 4.60 $\times$ 100 mm) specifically for the analysis of blue dyes. The system was controlled by the Empower 2 software. HPLC separation was performed at 35°C with a binary elution mixture composed of acetonitrile and bidistilled water containing 0.01%

(Continues)

FIGURE 1 (A, B) FT-IR spectra of samples. A, KBr pellets. B, ATR

trifluoroacetic acid (TFA). In function to the column employed, two gradient programs were used as following:

Chromatographic analytical gradient 1 for S4 and S5. Flow = 0.7 mL min ⁻¹							
Time (min)	0	10	12	22	32	40	50
% MeCN	30	50	70	90	90	100	100
% H ₂ O (0.01% TFA)	70	50	30	10	10	0	0
Chromatographic analytical gradient 2 for S3 and S6. Flow = 1.0 mL min ⁻¹							
Time (min)	0	0.6	1	3	3.5	10	
% MeCN	30	30	80	80	100	100	
% H ₂ O (0.01% TFA)	70	70	20	20	0	0	

The chromatograms were acquired respectively at the maximum absorption wavelength of 285 nm for blue dyes from indigo origin and, at 350 nm for the other yellow and

red dyes, to enhance the performance of the detection system. For information, 1 cm⁻¹ = 1.10⁷ nm.

Each sample was injected in triplicate.

2.5 | Identification and references

The characterization of each sample was conducted from references or commercial standards by determining the specific chromatographic and spectral fingerprints of materials, in the aim of deducing, as precisely as possible, the main composition of dye and/or pigment, as well as their origin. The references used are made of main dyes purified or isolated in several dye plants including *Lawsonia inermis* (henna), *Indigofera tinctoria* (indigo), *Philenoptera cyanescens* (liana indigo), *Khaya senegalensis* (African mahogany), and *Tectona grandis* (teak). All of these plants were studied as a prelude to this work.⁵ About

FIGURE 2 Chromatogram at 285 nm of samples S3 and S6 and UV-visible spectrum of identified compound with gradient program 1

50 commercial standards were purchased corresponding to phenolic, flavonoidic, and quinonic structures.

3 | RESULTS AND DISCUSSION

3.1 | Stratigraphy

The structure of the samples can be observed by using binocular microscopy. S1 reveals a thicker blue mass, supported by yellow crystals. The brown red layer is slightly thicker at the sample S2, while S3 and S5 exhibit a very thin layer of dye stuck to the wood. The sample S4 is constituted of two layers; a bottom red layer and a blue top one. These observations initially demonstrate the diversity of ethnic objects dyeing techniques. Furthermore, the application of dyes in specific locations of the object including color affixed to the head of S3 twins and back fetish S4, denotes a knowledge encoded¹⁵ which reveals that their role goes beyond the only decorative. In fact, this observation corroborates that of Bleton et al.,¹⁶ showing that these combined materials give life to the subject and contribute to its identity.

3.2 | Dyes analysis

3.2.1 | FT-IR analysis and microchemical tests

The FT-IR spectrum of the sample S1 shows a broad and intense band between 1114 and 1008 cm^{-1} characteristic of stretching vibration bonds of Si—O—Si and Si—O—Al, with a weak band at 1632 cm^{-1} and a broad band at 3457 cm^{-1} , respectively, characterizing the deformation and elongation vibrations of OH bonds. These bands are characteristic of synthetic ultramarine (laundry blue). However, only the natural ultramarine blue from Afghanistan/Badakhshan presents in addition, a low band in 2340 cm^{-1} characteristic of sulfide ions elongation⁸ which was not observed in this spectrum, confirming that it is of synthetic origin. In addition, this spectrum shows characteristic absorption bands of iron oxide at 538 and 470 cm^{-1} assigned respectively to a deformation beyond the

plane, the OH group and a vibration Fe—O, preceded by two shoulders observed at 3695 and 3619 cm^{-1} . This could be linked to the compactness of the blue pigment taking with an under-layer of iron oxide yellow ochre (Figure 1A,B).

Sample S2 shows very characteristic bands of iron oxide at 3696 and 3620 cm^{-1} and between 539 and 470 cm^{-1} . Another weak band is observed at 3438 cm^{-1} , traducing a red pigment from iron oxide hematite.

The sample S3 presents a typical spectral profile of cyan-blue, an equivalent of Prussian blue. It is characterized by a systematic stretching vibration of the triple bond C≡N at 2091 cm^{-1} that appears in a very intense band.¹⁷ Low characteristic absorption bands are observed corresponding to elongation vibration Fe—N at 604 cm^{-1} and, Fe—C bonds and C—Fe—C or Fe—CN at 499 cm^{-1} . Characteristic water bands appear at 3442 and 1639 cm^{-1} , respectively, corresponding to stretching vibration and deformation of the OH group.

The spectrum of the sample S4 shows three main groups: the OH group with a broad and intense band at 3441 cm^{-1} , similar to OH engaged in an intermolecular bonding (such as some alcohols) and, the CH group with a weak band at 2926 cm^{-1} characterizing the stretching vibration and the C=O at 1738 cm^{-1} also corresponding to a stretching vibration. The absorption bands observed at 1243 and 1033 cm^{-1} can be attributed to C—O and C—N bonds. So the sample S4 contains an organic blue dye.

Except for the band at 1738 cm^{-1} attributed to the vibration of the C=O bonds, the spectrum of the sample S5 has very similar bands to those of the sample S4: an intense band at 3441 cm^{-1} , similar to OH engaged in an intermolecular bonding and, the CH group with a weak band at 2926 cm^{-1} characterizing the stretching vibration. The absorption bands observed at 1632 and 1033 cm^{-1} can be attributed to C=O (β -diketone/enol) and C—O bonds. These comments show the presence of organic compounds in the sample.

Moreover, the S6 textile sample analyzed in ATR mode (Figure 1B), presents characteristic absorption bands of the natural cellulosic material (textile) with an intense band at

FIGURE 3 (A, B) Chromatogram at 350 nm of samples S4 (A) and S5 (B) and UV-visible spectra of identified compounds with gradient program 1

about 1109 cm^{-1} due to CO and a broad band at 3339 cm^{-1} related to the OH group and, a low band at 2920 cm^{-1} due to C—H. These results are in accordance with linen and cotton references, both naturally rich in cellulose, unlike the observation made with the referenced wool support.

However, it should be mentioned as cotton is a major part in the weaving in black Africa while flax is found in colder regions.⁵ It is important to note that the specific absorption band observed around 1008 cm^{-1} reveals competition from asymmetric stretching vibration characteristics of Si—O and Si—O—Al kaolin, a mineral widely used as pure or as additional charge in pigments.

Microchemical tests have revealed the presence of ferric and ferrous ions, the constituents of iron oxide in the samples S1 and S2. In addition, the presence of iron components of the characteristic blue ferric ferrocyanide was also confirmed. It is the same for Al^{3+} , Na^{+} , and S^{2-} ions, detected in the blue pigment S1 whose FT-IR spectrum characterizes

the vibrations of Si—O—Si bonds and Si—O—Al associated with synthetic ultramarine blue or bluing agent. Moreover, the microchemical analysis of the brown red sample S2 revealed in addition to iron, the presence of sulfides S^{2-} . This pigment could be from an area rich in iron oxide and

TABLE 2 Main results

Sample	Ion or molecule	Identification
S1	Al^{3+} , S^{2-} , Fe^{3+} , Fe^{2+} , Na^{+}	Mixture of synthetic ultramarine blue (blue washing powder) and iron oxide (yellow ochre)
S2	Fe^{3+} , Fe^{2+} , S^{2-}	Mixture of red iron oxide and pyrite
S3	Fe^{3+} , Fe^{2+} and indigotin	Mixture of Prussian blue (synthetic) and organic blue <i>P. cyanescens</i> (liana indigo)
S4	Indigotin and Lawsone	Liana indigo (upper layer) Henna (underlayer)
S5	Lawsone, apigenine	<i>L. inermis</i> (henna)
S6	Indigotin	Liana indigo

FIGURE 4 (A, B): *Lawsonia inermis* (A) et *Philenoptera cyanescens* (B) (L. Fagbohoun[©])

pyrite (FeS_2). Indeed, pyrite is a mineral that is widespread in the mangroves of southern Benin¹⁸; in the dry season, it appears everywhere on the surface of many deep desiccation cracks.¹⁹

3.2.2 | Chromatographic analysis

Samples S4 and S5 were analyzed in LC with the RP-18 column (gradient program 1) and S3 and S6 samples with the core-shell particles column (gradient program 2). Identifications were made according to the retention time and the UV/Vis spectrum by comparison with standard molecules.

The liquid chromatography coupled to a photodiode array detector analysis of blue samples from Ibeji twins (S3) and textile (S6) show the main presence of indigotin ($t_R = 7.33$ minutes) (Figure 2). Indirubin and flavonoids are not detected. Two species of indigo plants, *I. tinctoria* and *P. cyanescens*, are used in dyeing in Benin.⁶ The indigo plant origin determination was conducted via the study of the ratio of the relative content of indigoïds (indirubin/indigotin) in plant original matrix.⁵ Indeed, the absence of indirubin, structural isomer of indigotin and, markers of degradation (isatin and anthranilic acid) both indigoïds, show the high content of indigotin from initial species used.^{5,20} A preliminary study of indigo indicates that *P. cyanescens* contains a higher part of indigotin than *I. tinctoria*. So the indigo plant concerning this sample seems to be liana indigo and, this result corroborates the preliminary ethnobotanical study,⁶ showing that the frequency of use of *P. cyanescens* due to its richness in indigotin, is twice greater than that of *I. tinctoria*.

Concerning the sample S4, the chromatogram (Figure 3A) shows the presence of lawsone (2-hydroxy-1,4-naphthoquinone; $t_R = 15.1$ minute) biochemical marker of henna (*L. inermis*). Flavonoids usually present in this botanical species and, very sensitive compounds environmental factors, are not detected. Another dye is identified corresponding to indigotin compound

($t_R = 25.7$ minutes). The latter comes from the upper blue stratigraphic layer of the sample and shows a mixture of henna and indigo plant (probably *P. cyanescens*) in the dyeing of the object at the sampling location.

Chromatographic analysis of sample S5 shows the presence of lawsone and apigenine ($t_R = 22.5$ minutes), both present in *L. inermis* (Figure 3B).^{5,21,22}

It appears that lawsone is mainly characterized in samples containing red dye while blue samples are labeled with indigotin.

4 | CONCLUSION

Table 2 summarizes the main results of the different analyses. Indeed, among the six samples, S1 and S2 samples contained mineral matter whose laundry blue, a synthetic pigment imported, whereas dyes S4, S5, and S6 were composed of organic molecules including lawsone and indigotin, defining the dye plant, respectively, *L. inermis* (Figure 4A) and *P. cyanescens* (Figure 4B). Furthermore, the S3 sample was a mixture of organic blue (indigo) and synthetic mineral blue, Prussian blue. These materials were applied in thin layer or as a solid and compact mixture. Although the proportion of pigments in the mixture or in the composition of the layers has to be evaluated, giving important results for the restoration of these objects. It is also interesting to note that the identification of synthetic pigments such as laundry blue and Prussian blue in the mask S1 and the twins S3, shows that these objects have been probably realized later than 1800.

The different investigations conducted by FT-IR, microchemical tests and HPLC-PDA, brought important and necessary information for the identity and the restoration of these cultural heritage objects. Thus, through the identification of mineral particles or principles specific dyes, mineral

origin and/or botanical of museum specimens sampled were characterized. Indeed, the most widely employed red dye species and identified in the samples was *L. inermis* whereas *P. cyanescens* likely characterized blue samples studied. In addition, mineral pigments, mainly yellow and red ochers as iron oxides and synthetic pigments such as laundry blue and cyan-blue, were found. Thus, in the case of a future restoration of these objects, this work will permit a better knowledge concerning their original characteristics without disguising their original value in the process of their restoration. An investigation of the dating of the pigments used has to be considered in the perspective of an additional identifying data of these artifacts.

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CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interest with the content of this article.

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REFERENCES

- [1] de Balbín Behrmann R, Alcolea González JJ. Les colorants de l'art paléolithique dans les grottes et en plein air. *Anthropologie*. 2009;113:559-601.
- [2] Valeur B. La chimie crée sa couleur sur la palette du peintre. La chimie et l'art, le génie au service de l'homme. *L'Act Chim*. 2010;129-167.
- [3] Pegg DA, Hulme AN, McNab H, Quye A. Towards the identification of characteristic minor components from textiles dyed with weld (*Reseda luteola* L.) and those dyed with Mexican cochineal (*Dactylopius coccus* Costa). *Microchim Acta*. 2008;162(3-4):371-380.
- [4] Romeggio C. Sièges Rituels Yoruba. Questions de Conservation-Restauration, Entre Contexte Africain et Recontextualisations Occidentales [master's thesis in conservation-restoration]. Ecole Supérieure d'Art d'Avignon; 2007.
- [5] Fagbohoun L. Etude Chimique de Colorants Naturels et Matériaux Résineux Traditionnels du Bénin dans le Domaine Artisanal [PhD thesis]. Abomey-Calavi University, Avignon University; 2014.
- [6] Fagbohoun L, Gbaguidi AF, Ayedoun MA, Mathe C, Moudachirou M, Vieillescazes C. Etudes ethnobotanique et phytochimique des plantes tinctoriales sources de colorants naturels et matériaux résineux traditionnels du Bénin dans le domaine artisanal (Ifangni/ Bénin). *Ethnopharmacologia*. 2014;52:56-66.
- [7] Low MJD, Baer NS. Application of infrared Fourier transform spectroscopy to problems in conservation. *Stud Conserv*. 1977;22:116-128.
- [8] Derrick MR, Stulik D, Landry JM. *Infrared Spectroscopy in Conservation Science. Scientific Tools for Conservation*. Los Angeles: The Getty Conservation Institute; 1999.

- [9] Charlot G. *Analyse Qualitative Rapide des Cations et des Anions*. 4th ed. Paris: Dunod; 1980:96.
- [10] Odegard N, Carroll S, Zimmt SW. *Material Characterization Tests for Objects of Art and Archaeology*. 2nd ed. London: Archetype Publications; 2005:240.
- [11] Quye A, Wouters J. An application of HPLC to the identification of natural dyes. *Dyes Hist Archaeol*. 1991;10:48-54.
- [12] Surowiec I. Application of high-performance separation techniques in archaeometry. *Microchim Acta*. 2008;162(3-4):289-302.
- [13] Philippon J. *Microanalyse Chimique des Pigments et des Liantes par Voie Humide*. France: Institut Français de Restauration des Oeuvres d'art; 1986.
- [14] Bourhis K, Blanc S, Mathe C, Dupin JC, Vieillescazes C. Spectroscopic and chromatographic analysis of yellow flavonoid lakes: quercetin chromophore. *Appl Clay Sci*. 2011;53:598-607.
- [15] Bleton J, Sansoulet J, Rivallain J. Analyse d'objets africains par chromatographie gazeuse couplée à la spectrométrie de masse. *Analisis*. 1996;24(7):28-31.
- [16] Bleton J, Rivallain J, Sansoulet J. Caractérisation et fonctions d'enduits placés sur les masques Ejumba de basse Casamance, sud du Sénégal. *J Agric Trop Bot Appl*. 1995;XXXVII(2):25-35.
- [17] Feller RL, Johnston-Feller RM, Cologne VB, earth K. In: FitzHugh EW, ed. *Artists' Pigments. A Handbook of Their History and Characteristics*. Vol 3. Washington, DC: National Gallery of Art; 1997.
- [18] Vieillefont J. Contribution à l'Étude de la Pédogenèse dans le Domaine Fluvio-Marin en Climat Tropical d'Afrique de l'Ouest [Thèse]. Université Paris VI; 1977.
- [19] Gaillard M, Lang J, Lucas J. Etude sédimentologique des milieux de mangrove du Bénin occidental (Afrique de l'Ouest). *Oceanol Acta*. 1982;N°SP:129-138.
- [20] Rodriguez ES, Rodriguez AA, Garcia MA, Camara RC. Characterization of natural and synthetic dyes employed in the manufacture of Chinese garment pieces by LC-DAD and LC-DAD-QTOF. *E-Conserv Mag*. 2011;21:38-55.
- [21] Dixit SN, Srivastava HS, Tripathi RD. Lawsone, the antifungal antibiotic from the leaves of *Lawsonia inermis* and some aspects of its mode of action. *Indian Phytopathol*. 1980;31:131-133.
- [22] Afzal M, Al-Oriquat G, Al-Hassan JM, Muhammad N. Flavone glycosides from *Lawsonia inermis*. *Heterocycles*. 1980;14:1973-1976.

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