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Blue to black: Hypotheses on plant use complexity in traditional dyeing processes in Southeast Asia and China

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ABSTRACT

Modern indigo dyeing is achieved using chemical dye vats with toxic reducing agents that have an impact on the environment and human health. Consequently, there has been interest in traditional indigo dyeing processes and their potential for more environmentally friendly industrial production. Traditional indigo dyeing was studied by conducting a literature review (China, India, Indonesia, the Philippines, and Vietnam) and field surveys (Timor Leste, Indonesia, Laos, and China) in Southeast Asia and China (SAC). Traditional SAC blue and black dyeing processes can be a combination of separate dyeing steps. Here, we documented plant species and ingredients in the blue to black dyeing processes used in addition to indigo yielding species. We recorded 80 plant species belonging to 39 families and 67 genera used in the "blue to black" dye processes in SAC. Owing to local use and phytochemicals or microbial substances of these species and their function in the dyeing processes, eight hypotheses for added species, including lime or ash water, microorganisms, food for microorganisms, electron donors, electron mediators, reducing sugars, metallic mordants, and tannins were suggested herein. The combination of hypotheses was supported by the findings and theories of previous studies and clarifies why these particular plant species are likely added to dye vats. The hypotheses and theories derived from this study pave the way for insights into indigo dyeing processes that reduce inorganic chemical additives using additional plant products, which consequently may provide a green route for cleaner production strategies. This research identifies gaps in knowledge and highlights where further work is needed to verify the hypotheses proposed for adding products to dye vats in the future.

1. Introduction

Indigo, sourced from at least 31 plant species in eight families, is one of the oldest pigment dyes in the world (Cardon, 2007), with recent archaeological evidence of indigo-dyed textiles from at least 6000 years ago (Splitstoser et al., 2016). Since the invention of synthetic indigo at the end of the 19th century, the use of natural indigo has plummeted (Prasad, 2018). By 2011, 50,000 tons of indigo dye were reported to be produced per year, 95% of which was used to dye more than four billion denim textiles produced annually (Hsu et al., 2018). Indigo is one of the major classes of redox (vat) dyes that are insoluble in water, yet can be reduced (Pricelius et al., 2007). In industrial indigo dyeing, the most commonly used reducing agent to convert indigo pigment into a water-soluble leuco-form is sodium dithionite ($Na_2S_2O_4$), raising concerns about environmental pollution due to sulfates and sulfites in wastewater (Saikhao et al., 2018). A growing interest in "green chemistry," "green fashion," and policy initiatives to minimize negative impacts of chemical pollutants have stimulated scientific interest in traditional indigo dyeing processes globally (Franssen et al., 2010; Muthu and Gardetti, 2016a, 2016b).

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Traditional indigo dyeing is still practiced in various forms worldwide, using natural organic additives to dye vats without the use of toxic chemicals. However, traditional indigo dyeing is a complicated fermentation process, with different recipes used by master dyers from different regions and ethnic groups. Even within the same region, there are variations in these recipes and diverse additives. For example, in Japan, the *sukumo* (composted indigo) fermentation vat uses a mixture of *sukumo* (generally from *Persicaria tinctoria* (Aiton) H. Gross), wood charcoal, wheat bran, and rice wine (Aino et al., 2010). Similar procedures are conducted for indigo dyeing in India, which involves the addition of indigo, slaked lime, and treacle (Mohanty et al., 1987). Products traditionally added to indigo dye vats (besides indigo-yielding species) have not been well studied. A reason for this, based on field experience in Indonesia and Timor Leste (Cunningham et al., 2014), is that traditional dyers are often reluctant to discuss the details of the plants added to indigo dye vats. This traditional knowledge is almost exclusively held by women. A few studies have been conducted on products added to indigo fermentation vats in Southwest China (Li et al., 2019), Europe (Cardon, 2007), South Asia (Mohanty et al., 1987), Indonesia (Hofmann, 1997; Jasper and Pirngadie, 1912), and Thailand (Krikorian, 1994). The underlying theories of traditional indigo dye processes are complex and diverse (Aino et al., 2018; Blackburn et al., 2009; Chavan, 2015; Nicholson and John, 2005; Vuorema, 2008), and a systematic theoretical framework is needed to understand why particular ingredients are added.

Southeast Asia and China (SAC), including Timor Leste, India, Indonesia, Laos, the Philippines, and Vietnam, are global "hotspots" of indigo-producing plant diversity. Fermentation vats are still used by several minorities, as well as a broad range of additional plant species and ingredients (Cardon, 2007). Therefore, the aim of this study was to document the broad range of species added to indigo dyeing processes in various regions of SAC through a literature review and field research. For the first time, this research develops an explanatory model of traditional blue-to-black dyeing processes to encourage future research on the application of environmentally friendly dyeing techniques.

2. Methods and approach

2.1. Literature review

We conducted a literature review to extract pertinent data from previous studies involving traditional blue-to-black dyeing processes conducted in China, India, Indonesia, the Philippines, and Vietnam. Data extraction was used to collect information on the phytochemicals or microbial substances of each plant species added to the dye vats. Finally, data concerning the functions of collected phytochemicals or microbial substances were extracted. We developed a comprehensive search strategy to identify relevant studies, and the format of the search string was compatible with each database (Table S1). Searches were performed using different electronic databases, i.e., Web of Science, SCOPUS, CNKI (China National Knowledge Infrastructure), and Google Scholar.

Using the search terms documented in Table S1, 1207 articles and books were selected and are listed in the Supplementary Information. Of these, eight studies have detailed information on the additional plant species in traditional blue and black dyeing processes and 136 scientific publications have described the related mechanisms or theories of these processes. Furthermore, 638 studies presented the phytochemicals or microbial substances of each plant species that were added to the dye vats. Moreover, 496 studies mentioned the functions of the collected phytochemicals and microbial substances.

2.2. Field research

To validate and supplement the results of the literature review, we conducted periodic ethnobotanical fieldwork on plant species added to traditional blue-to-black dyeing processes in Timor Leste (2009), Indonesia (2016–2019), Laos, and China (2016–2020). This included key informant interview surveys (Timor Leste, Indonesia, Laos, China) and household interviews in Hunan, Hainan, and Yunnan provinces (China). The ethnic minorities (Dong, Li, Miao, and Hani people) in these Chinese provinces have a history of cultivating indigo plants and processing indigo dye for dyeing their traditional textiles. We interviewed 41 key Chinese informants between July 2018 and November 2019. The ethnobotanical records of plants used in Timor Leste, Laos, and Indonesia were less structured and based on 10 –30 key informant interviews in each location over an extended duration. Appendix A presents the questionnaire used during the interviews. We comprehensively recorded the process of traditional indigo dyeing techniques according to interviews with master dyers. We also documented ethnobotanical information for each plant species, including scientific names, parts used, and the reason for local use. The information on plant species used is summarized in Appendix B. Voucher specimens of several species listed here were collected and deposited at the herbarium of the Kunming Institute of Botany in China or in the herbarium of the Bebali Foundation in Indonesia.

2.3. Data analyses

To compare the knowledge gathered from each region, statistical analyses were performed using R software (version 4.1.1). Sankey plots were generated using the "group_by" function in the dplyr package and the "to_lodes_form" function in the ggalluvial package, and subsequently plotted using the ggplot2 package (Brunson, 2018). The keywords of 136 scientific publications describing related mechanisms or theories of indigo dyeing processes were extracted using EndNote 8.0, and subsequently calculated and visualized at https://worditout.com/word-cloud/create. Extracted plant data were qualitatively summarized based on phytochemicals or microbial substances and their functions. Based on data analysis and existing studies on the mechanisms of indigo dyeing processes, we proposed eight testable hypotheses on why certain ingredients are added to dyeing processes. Thus, we suggested an explanatory model of traditional blue-to-black dyeing processes in SAC.

3. Results

3.1. Traditional blue to black dyeing processes in SAC

Traditional SAC blue-to-black dyeing processes are generally divided into two steps. Indigo dyeing was performed first (achieved blue hue), followed by an overdyeing process (achieved black hue). We also provided percentages (and numbers) of respondents from each village that preferred specific indigo shades from our field research in China (Table S2). It showed that dark blue or black colors are culturally preferred by the local people in these Chinese areas.

Based primarily on literature and verified secondarily through field studies, we found that in addition to a variety of indigo source species, 80 plant species belonging to 39 families and 67 genera were used as additives in SAC blue-to black dye processes, of which 31 plant species were used as additives in indigo dye vats and 29 plant species were used for the separate overdyeing process. Furthermore, 20 plant species have been recorded in previous studies; however, use information was absent. Among them, 47 plant species were documented during the field research, whereas 33 plant species were recorded in the literature reviewed (Appendix B).

In the first step of the SAC dye process (indigo vat dyeing), the use of plant additives was only found in China, Indonesia, and Timor Leste. In the second step process (overdyeing), plant additives were used in Indonesia, China, Timor Leste, India, the Philippines, and Laos (Fig. 1). Only *Bridelia monoica* (Lour.) Merr. is used in Vietnam from the literature review, and did not report any use information (vat or over), as a

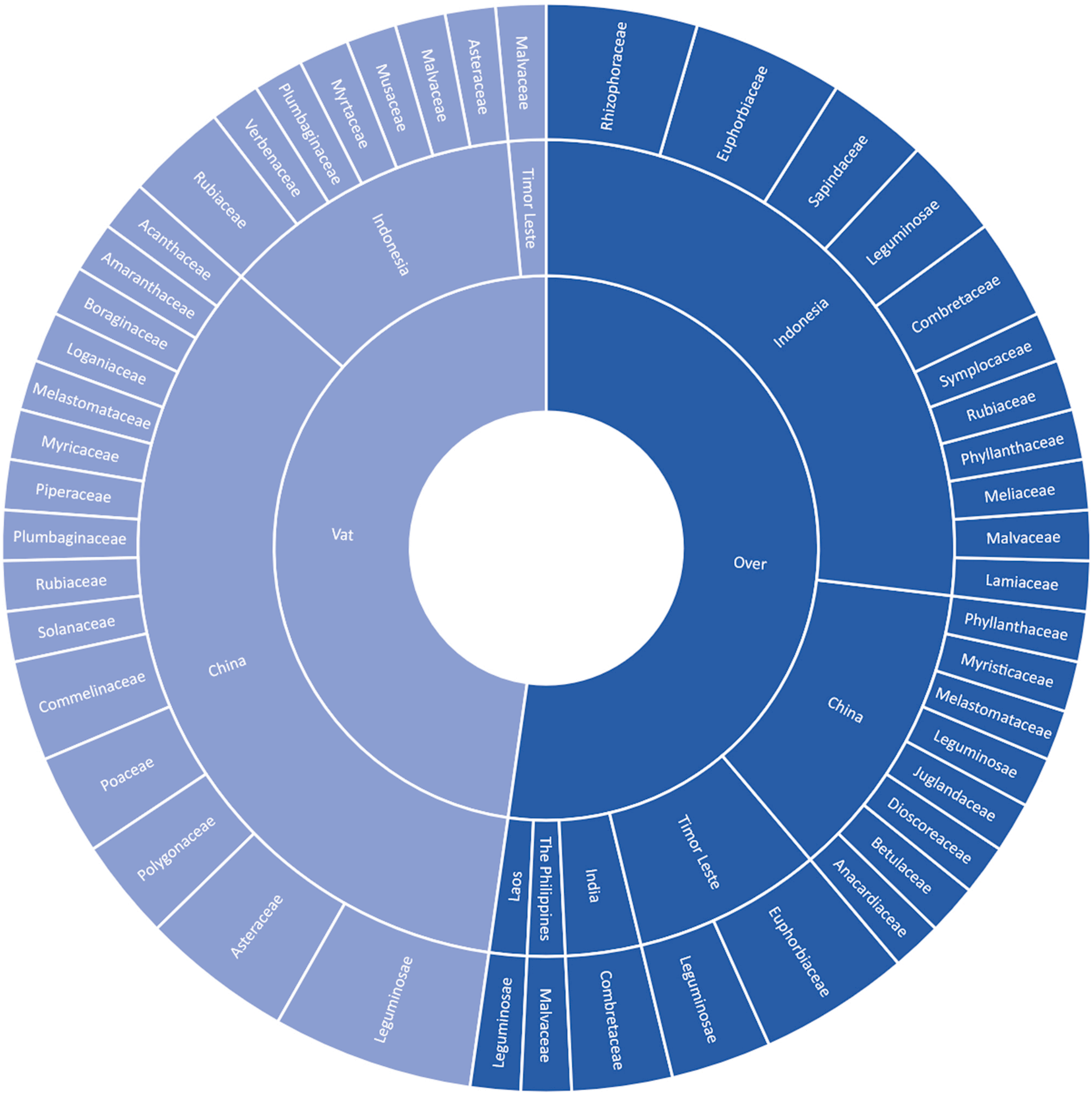

Fig. 1. The classification and analysis of plant species added during SAC dye processes (Note: Vietnam does not appear in the findings because the literature review lacks the use information of the recorded plants). The inner ring shows the two steps of the dyeing processes (indigo vat and overdye). The middle ring reveals the included countries use which step of the dyeing process. The outer ring outlines the plant families use by which country at which step of the dyeing process.

result Vietnam did not appear in the Fig. 1, but its absence did not affect the results. Moreover, plant species from 15 families were used during the indigo vat dyeing process in China, with the most abundant families being Leguminosae and Rubiaceae. Plant species from 11 families were used during the overdyeing process in Indonesia, with Rhizophoraceae and Euphorbiaceae families being the most abundant. Euphorbiaceae was the most abundant plant family added during the overdyeing process in Timor Leste, followed by Leguminosae.

3.2. *Seven reasons for using plant additives in dye processes*

The use of different plant additives in each country revealed distinct dyeing characteristics across SAC geographic areas. Among the reasons for using plant additives in traditional SAC dye processes, achieving black and fermentation recipes were considered to be the most indispensable factors during the blue and black dyeing processes (Fig. 2). However, there is an uneven distribution of reasons for using plant additives in different countries. Seven reasons have been documented in China. Similar patterns were also observed in Indonesia. Adding plant species to bring good luck to indigo dye vats, adding plant species to increase the color fastness, and adding plant species to accelerate the fermentation process were more common in China and Indonesia compared with other countries. Adding plant species to achieve black, was ubiquitous across the SAC areas studied, while adding "fermented wine" at the start of indigo fermentation was only found in China. Moreover, the addition of lime (or ash lye) from various sources to increase the pH of dye vats is well known. Traditional indigo dyers increase the pH of indigo dye vats from a wide range of sources. Before the commercial availability of lime, this included the use of ash from specific plant species, burnt limestone, mollusk shells, or coral. In SAC,

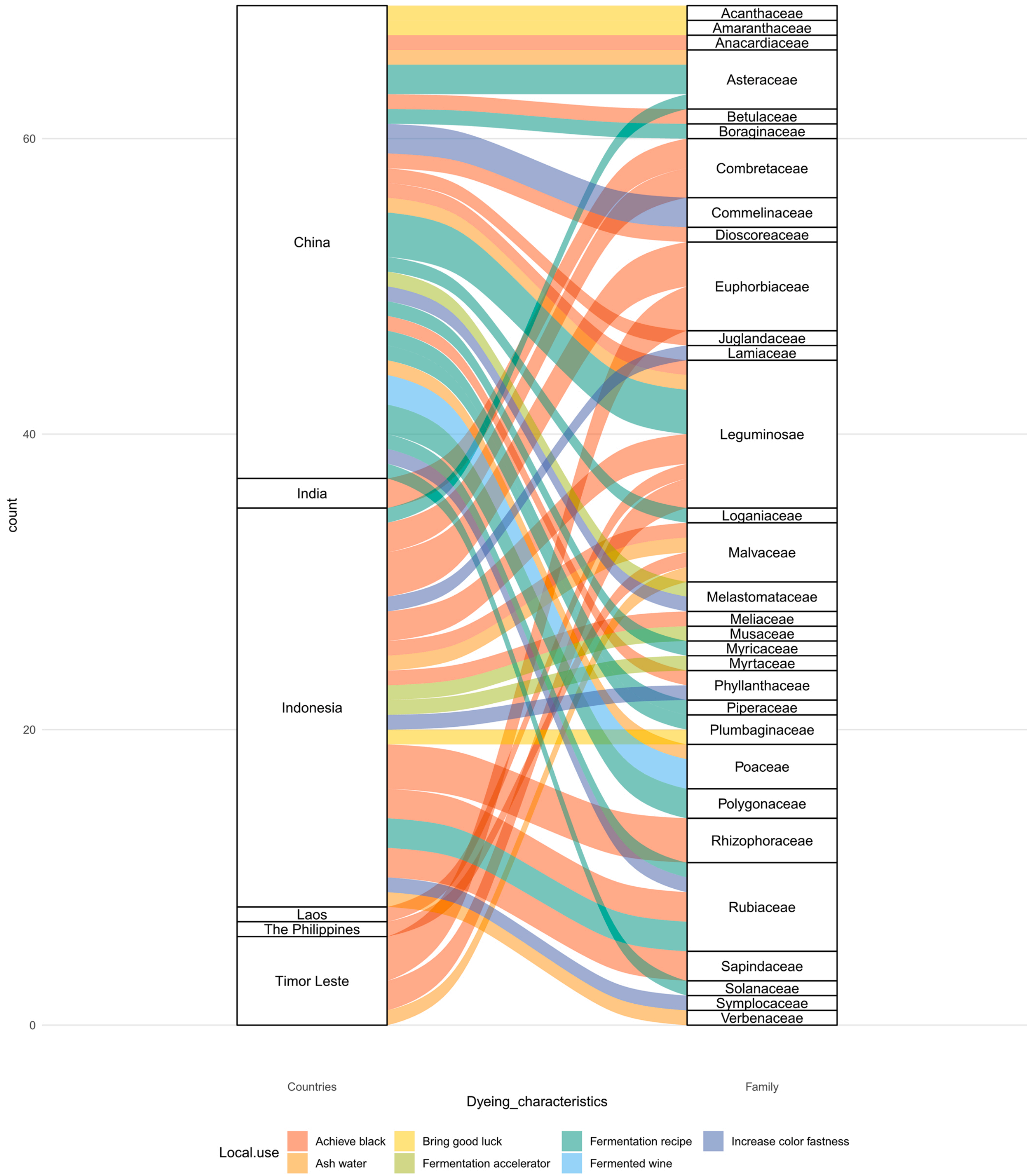

Fig. 2. Sankey diagram showing the comparison of the reasons for using the plant additives within each country (Note: Vietnam does not appear in the findings because the literature review lacks the use information of the recorded plants). Each rectangle in the left column represents a study area (Countries), and each rectangle in the right column represents a plant additive (Family level). The lines represent which country use which plant additive for which reason in the blue to black dyeing processes, and each reason has a distinct color. The thickness of the lines indicates the number of plant species in each family.

traditional sources of lime or ash depend on the location and ecological conditions where the indigo dyers live or on trade networks. Where indigo dyers live in karst landscapes, limestone is readily available for burning. Coral or marine mollusks, such as oysters or clam shells, are used on ocean coasts. In inland Chinese and Indonesian villages, plant ash or shells of freshwater snails collected from rice paddies and burned to produce alkaline ash (Fig. 3).

Fig. 3. Sources of alkaline water for different SAC indigo vats. **A.** Filtering water through a sack filled with ash from rice straw (Landian Yao, Yunnan, China). **B.** Burning rice straw for alkaline ash before filtration (Hmong, Guizhou, China). **C.** Bauhinia variegate L., one of several species selected to be burnt for good quality ash to produce "ash water" (Landian Yao, Yunnan, China). **D.** Freshwater snails burnt with rice straw which is then to make a high pH dye vat (Timor Leste). **E.** A pot of slaked lime sourced by from burning limestone (Dai, Jinghong, Yunnan, China). **F.** A plastic bucket of rice straw after filtration of "ash water" (Highland Miao, Hainan, China). Photos: A. B. Cunningham.

3.3. Analysis of the existing indigo dyeing mechanisms

We summarized existing studies of indigo dyeing processes to present the status and emerging trends of its mechanisms. Various keywords are covered in the existing mechanisms or theories of indigo dyeing processes, with a strong focus on reducing agents, redox mediators, indigo reduction, alkaline solutions, microbial reduction, and indigo-reducing strains (Fig. S1). Indigo pigment is insoluble in water and barely penetrates the fiber; however, it can be reduced to its soluble form, leuco-indigo, under alkaline conditions. Microbial reduction is the most attractive reduction method, and to date, 15 indigo reducing Gram-positive anaerobic bacteria have been identified and isolated from woad dye vats (Europe), indigo dye vats (South Korea), and *sukumo* dye vats (Japan) as shown in Table S3. Meanwhile, attempts have been made to use organic reducing agents, redox mediators, enzymes, or electrochemical reduction to enhance the reducing activity and improve colorfastness in emerging fields.

3.4. Chemical composition and efficacy analysis of added species

According to a literature search for each plant species added to indigo vats concerning their phytochemicals or microbial substances, 11 studies identified that *Musa acuminata* Colla was rich in reducing sugars (glucose and fructose), and 36 studies demonstrated that *Psidium guajava* L. was a good source of reducing sugars. Fifty-one studies described the endophytic microbial diversity of *Piper* sp., and nine studies indicated that the endophytes of *Reynoutria japonica* Houtt. were abundant and unique.

Twenty-two studies showed that diverse flavonoid compounds were extracted from *Buddleja officinalis* Maxim., seven studies revealed the presence of flavonoids in *Melastoma dodecandrum* Lour., 49 studies showed that flavonoid compounds are widely found in *Myrica rubra*

(Lour.) Sieb. & Zucc., seven studies reported the presence of flavonoids in *Kummerowia striata* (Thunb.) Schindl., 36 studies demonstrated that a number of flavonoid compounds have been isolated from *Persicaria hydropiper* L., and 25 studies showed that *Ageratum conyzoides* L. was rich in flavonoids (Fig. 4 A).

Nine studies reported that *Plumbago indica* L. was rich in quinone-based compounds, 58 studies indicated that *Reynoutria japonica* was a quinone-rich natural product, five studies reported that several quinone-based compounds were derived from *Tithonia diversifolia* (Hemsl.) A. Gray, four studies reported the presence of quinones in *Caesalpinia sappan* L., five studies described the presence of quinone-based compounds in *Dalbergia odorifera* T. C. Chen, nine studies indicated the presence of quinone-based compounds in *Carthamus tinctorius* L., and 68 studies showed that large quantities of quinones were found in *Morinda citrifolia* L. (Fig. 4B).

Furthermore, 175 studies indicated tannin-rich species, including *Homalanthus novoguineensis* (Warb.) K.Schum. (1), *Pterospermum niveum* Vidal (1), *Pterospermum diversifolium* Blume (1), *Schleichera oleosa* (Lour.) Merr. (1), *Uncaria elliptica* R. Br. ex G. Don (1), *Homalanthus populneus* (Geiseler) Pax (2), *Spatholobus suberectus* Dunn (2), *Cassia fistula* L. (3), *Alnus nepalensis* D. Don (4), *Terminalia bellirica* (Gaertn.) Roxb. (4), *Ceriops decandra* (Griff.) W.Theob. (5), *Ceriops tagal* (Perr.) C. B.Rob. (5), *Nephelium lappaceum* L. (5), *Macaranga tanarius* (L.) Müll.Arg. (6), *Platycarya strobilacea* Siebold & Zucc. (6), *Rhus chinensis* Mill. (6), *Xylocarpus granatum* J. Koenig. (6), *Dioscorea cirrhosa* Lour. (7), *Morinda citrifolia* (7), *Rhizophora mucronata* Lam. (11), *Terminalia catappa* L. (18), *Phyllanthus emblica* L. (26), and *Terminalia chebula* Retz. (47) (Fig. 4 C).

Twenty-two studies showed that aluminum hyperaccumulation is a distinctive trait in *Melastoma malabathricum* L. Three studies indicated that *Aporosa frutescens* Blume (1) and *Symplocos fasciculata* Roxb. (2) can accumulate aluminum. *Commelina bengalensis* L. showed a high level of tolerance to copper in five studies., Nineteen studies showed that *Commelina communis* L. has the highest copper accumulation ability, and three studies reported *Hyptis suaveolens* (L.) Poit. capable of Cu or Cr

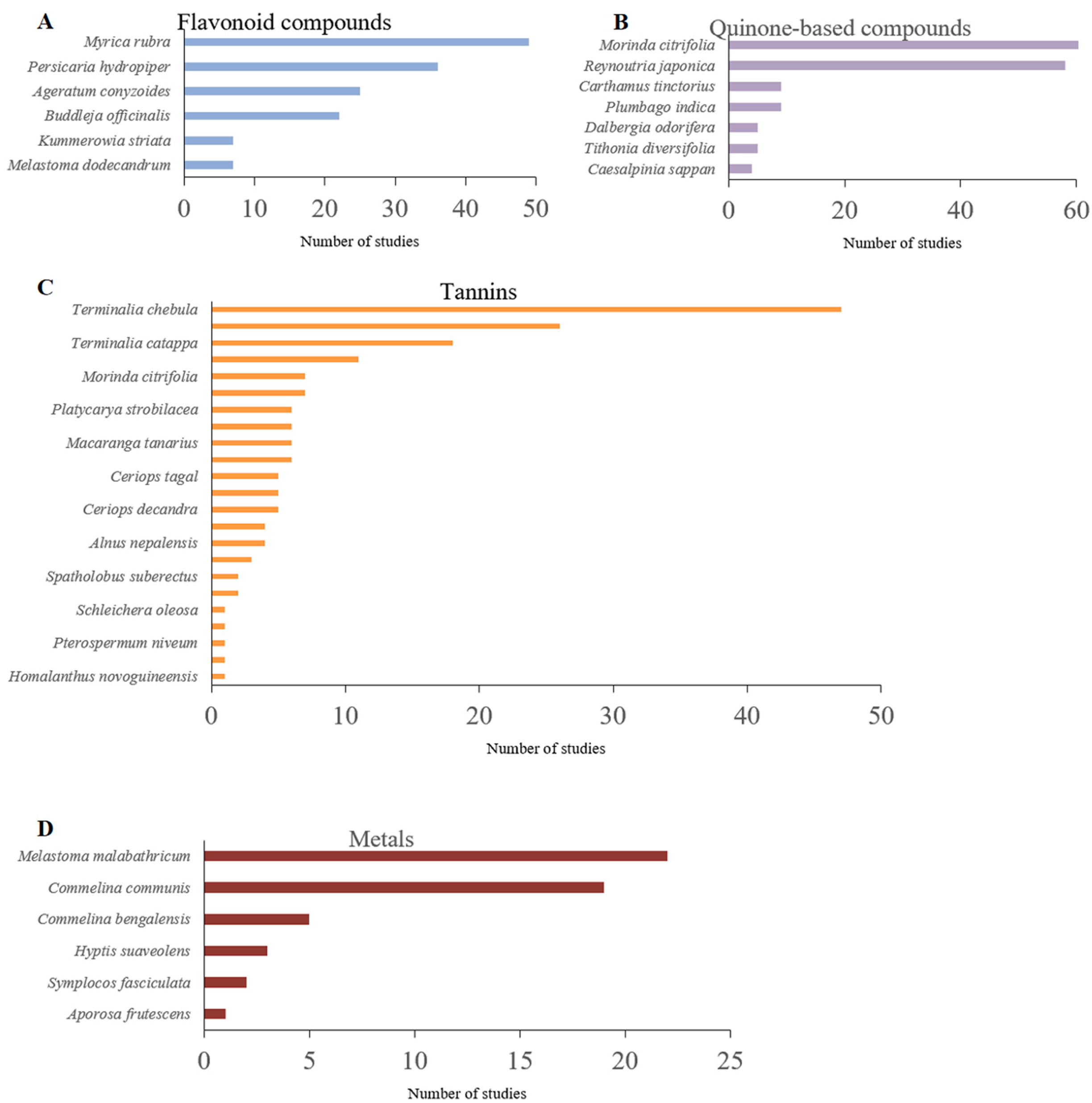

Fig. 4. Literature search for each plant species added to the SAC dye vats concerning their phytochemicals or microbial substances. **A.** Six species are rich in flavonoid compounds. **B.** Seven species are rich in quinone-based compounds. **C.** Twenty-three species are rich in tannins. **D.** Six species are aluminium, copper, or chromium hyper-accumulators.

accumulation and tolerance (Fig. 4D).

Based on the reasons for local use and chemical composition of plant additives in the traditional blue-to-black dyeing processes, of the 80 plant species added during SAC dye processes, five species were used as plant ash, three species as symbolic ingredients, two species as carbon sources, two species whose fruits were rich in reducing sugars, two species with a variety of plant endophytes, six species were flavonoid-enriched species, seven species had a high yield of quinone-based compounds, and six species were aluminum, copper, or chromium hyper-accumulators. In addition, 23 species had a high tannin content. Nine species had an uncertain chemical composition, and 22 species did not report any use information or phytoconstituents (Appendix B).

According to literature reviewed, four studies confirmed that rice leaves, rice wine, or wheat bran application was effective in providing an additional carbon and nutrient source for the growth of microorganisms. The fact that a combination of tannins and indigo resulted in black textiles was identified in only four studies. Nine studies were related to the effect of tannin mordanting on the coloring and functionalities of different fabrics. Glucose and fructose, which are the main reducing sugars, were tested as green alternative reducing agents for the indigo dyeing of cellulose fabrics in 13 studies. We examined 35 articles, in which plant ash was used as the source of alkali reagents to provide an alkaline environment. We also found 42 studies involving the use of metallic mordants, such as aluminum, copper, or chromium, to improve the dyeing effect with natural dyes. A wide range of indigo-reducing bacteria (Table S3) isolated from indigo fermentation vats play an important role in the indigo-reducing reaction (45 studies). In addition, 54 studies indicated that a range of flavonoids preferred to act as potential electron donors, and their electron-donating abilities were based on their structure. Moreover, 291 studies showed that quinone compounds have attracted great attention because of their unique function as redox mediators to facilitate electron transfer reactions and accelerate the reductive transformation (Fig. 5).

3.5. *Eight testable hypotheses of additives in dyeing processes*

From a chemical reaction perspective of indigo vat dyeing, it is easy to convert indigo dyes into their soluble form, leuco-indigo. The traditional indigo vat dyeing process is regarded as an alkaline anaerobic bioprocess, guided by scientific principles. The principles on which the multi-step process is based can be summarized into two aspects: alkaline environment and biological fermentation.

Based on the reasons for local use and the current studies related to the mechanisms or theories of indigo dyeing processes, combined with chemical composition and efficacy analysis of plant additives in the traditional blue-to-black dyeing processes, we suggested eight testable hypotheses that offer sustainable and environmentally friendly alternatives to modern indigo dyeing (Table 1).

4. Discussion

Traditional SAC blue and black dyeing processes include indigo vat dyeing and overdyeing. The former is relatively well studied, particularly in Europe and Japan (Balfour-Paul, 2011; Blackburn et al., 2009; Cardon, 2007; Hirota et al., 2013b; Tu et al., 2019b; Yumoto et al., 2008). The most detailed studies on the microbiology of indigo fermentation processes have been conducted on *sukumo* fermentation by *Polygonum tinctorium* Ait. in Japan (Tu et al., 2019b). However, the overdyeing process has not been extensively studied. Although indigo vat dyeing processes have complex recipes and are carried out in different parts of the world, they involve a chemical reaction that reduces indigo under alkaline conditions to leuco-indigo, which has a direct affinity with textile fibers (Blackburn et al., 2009) (Fig. S2). When the fiber is exposed to air, it can oxidize leuco-indigo back to insoluble indigo and is mechanically trapped within the fiber structure, so that the fiber is dyed blue (Blackburn et al., 2009).

An illustration is shown here to summarize the interaction and complexity of the traditional blue to black dyeing processes in the explanatory model on the basis of the following principles reviewed from the current studies (Fig. 6).

Table 1
Testable hypotheses.

Local use	Testable hypotheses	Categories	Steps
Ash water	Hydrolysis of plant ash in water to produce hydroxide ions	Alkaline environment	Indigo vat
Fermentation accelerator	Reducing sugars from fruits as reducing agent	Biological fermentation	
Fermentation recipe	Flavonoid compounds from plants as electron donators		
	Microorganisms from plants for microbial reduction		
	Quinone-based compounds from plants as electron mediators		
Fermented wine	Carbon source for reduction microorganisms		
Achieve black	Tannin-rich species combine with indigo to produce black	Mordants	Overdye
Increase color fastness	Hyper-accumulator plants act as metal mordants		

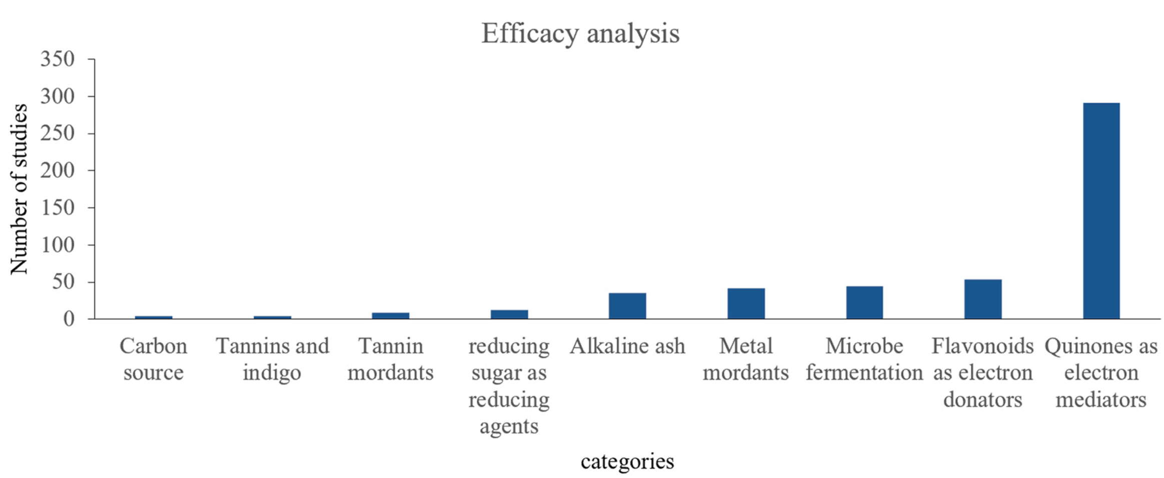

Fig. 5. The functions of phytochemicals or microbial substances derived from additional plant species.

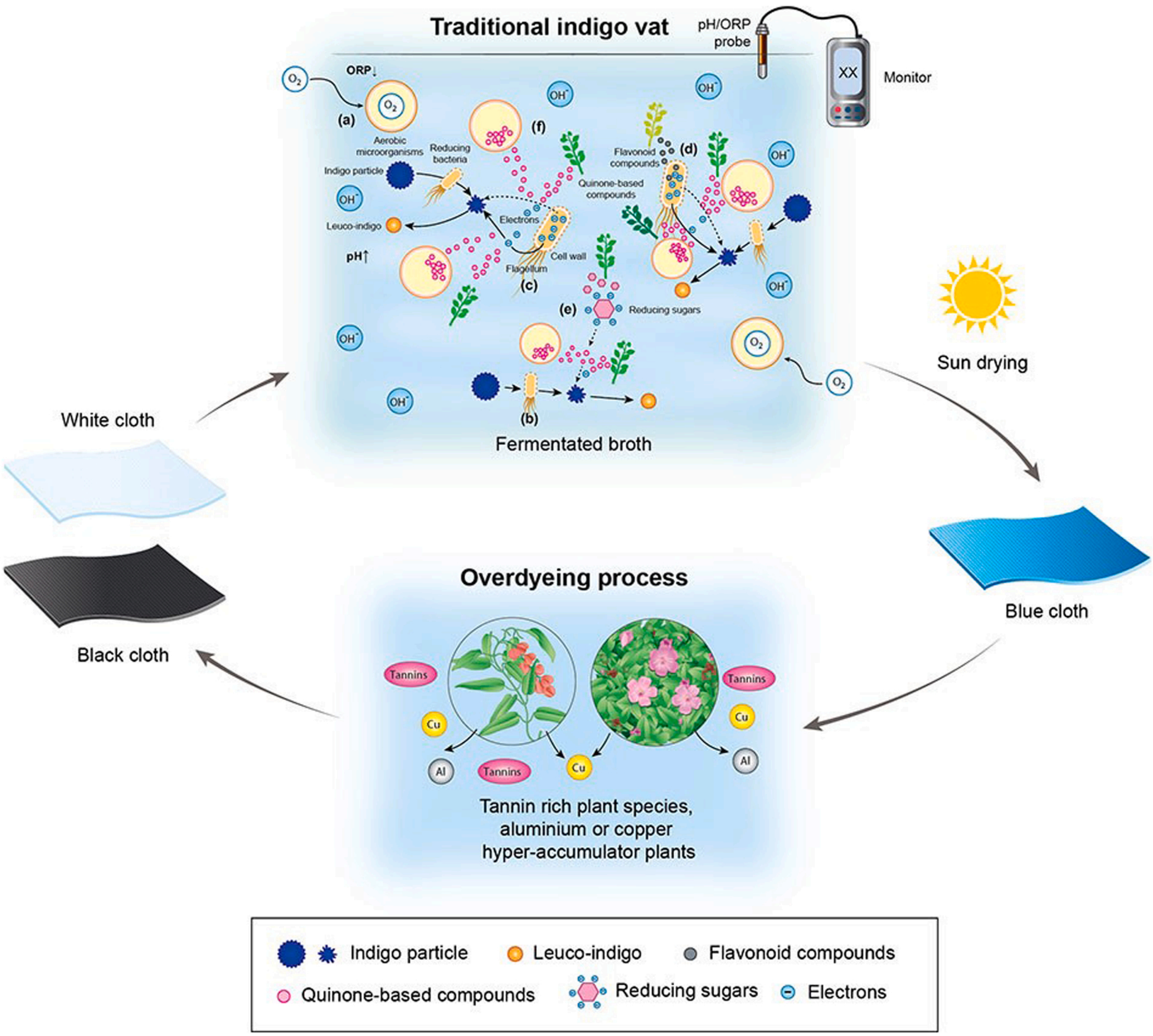

Fig. 6. Schematic diagram illustrating the theory of traditional dyeing process with an emphasis on the two units in order to correlate theory with practice. **(a).** The initial exhaustion of oxygen by respiration of aerobic microorganisms. **(b).** Reducing bacteria decrease the indigo particle size. **(c).** Reducing bacteria will transfer the electrons (metabolized by itself) from the inside of the cell to the solid electron acceptor (indigo) outside the cell through the cell wall or flagellum. **(d).** Flavonoid compounds (secreted by plants) can be absorbed and utilized by microorganisms as electron donors, then the electrons are transferred from the inside of the cell to indigo through the cell wall or flagellum. **(e).** Reducing sugars from plants act as electron-rich intermediators. **(f).** Quinone-based compounds are excreted by microorganisms or originated from plants that act as electron mediators between microbe cells and indigo particles.

4.1. Alkaline environment

The initial and most important step in the traditional indigo vat dyeing is pH control because of the diversity of reduced indigo according to the pH value in the solution (Baig, 2012). The acid form of leuco-indigo appears first, which is an off-white solid and has limited affinity with the fibers. The ionic form of leuco-indigo is derived from the further addition of alkali to the acid form of indigo, which can be divided into two forms: the mono-phenolate ionic and bi-phenolate ionic forms of leuco-indigo. They are both pale yellow liquids and readily absorbed by the fibers (Etters, 1995, 1993; Etters and Hou, 1991) (Fig. S2). The mono-phenolate ionic form has a higher affinity for textile fibers than the bi-phenolate ionic form (Etters and Hou, 1991). Hence, an alkaline medium plays a crucial role in the dissolution and adsorption of indigo in textile fibers (Son et al., 2019). As shown in Fig. S2, the traditional indigo dyeing process must be performed in an alkaline environment obtained by adding lime or ash water. The importance of an appropriate pH (generally 10.3–11) during indigo vat dyeing is also well known (Okamoto et al., 2017). However, the mechanisms by which the pH in the indigo dye vat influences other components, such as microbiology, enzymatic reactions, and the influence of metallic salts from Al hyperaccumulating plants remain unknown.

4.2. Biological fermentation

Microbial indigo reduction is accomplished in microbial communities through complex mechanisms that involve multiple biological factors. In this study, the reduction process consisted of partially dissolved indigo particles and insoluble indigo to soluble leuco-indigo, which was primarily driven by the microorganisms involved in the fermentation of dye vats (Suzuki et al., 2018).

Aerobic microorganisms generate a sufficient reducing potential for indigo through the initial exhaustion of oxygen by respiration (Fig. 6a). Aerobic microorganisms play an important role in the maintenance of microbial communities involved in the fermentation of dye vats. *Bacillus thermoamylovorans*, *Geobacillus palidus* and *Ureibacillus thermosphaericus*, are aerobic species that dominate, at least in the early stages of fermentation, in a woad vat performed in mediaeval Europe (John et al., 2008). Tu et al. examined the Japanese *sukumo* fermentation fluid, and the dyeing intensity increased dramatically on the 5th day following the initiation of fermentation, which might be initiated by the consumption of oxygen by aerobic microorganisms such as Bacillaceae (Tu et al., 2019a). The respiration of these aerobic bacteria consumes oxygen which allows the growth of fermentative, obligately anaerobic, indigo-reducing bacteria (Blackburn et al., 2009).

The mechanism of indigo dissolution could be achieved by bacteria that decrease the indigo particle size (Fig. 6b). In a previous study, smaller particles were reduced more easily than larger particles (Roessler et al., 2003a,b). The diameter of indigo particles is at least 50 times those of bacterial cells (Compton et al., 2000). Therefore, when indigo was incubated in the supernatant of a *Clostridium isatidis* culture, the average diameter of the indigo particles decreased from 35 μm to 3 μm (Nicholson and John, 2005). In addition to reducing the indigo particle size, the surface of the indigo particle can also be modified with anthraquinone to promote the reductive solubility of indigo to leuco-indigo. Electron microscopy of indigo crystals before and after reductive dissolution revealed that anthraquinone introduced a "wedge effect" to the crystal morphology, which can be adsorbed into the gap between indigo sheets and facilitate rapid breaking up of the solid crystal, thereby catalyzing the reduction (Vuorema et al., 2009).

The mechanism of indigo reduction includes the following three components:

(i) A stable microbiota for indigo reduction under alkaline anaerobic conditions. Indigo reducing bacteria change depending on the materials used (e.g., woad balls, indigo paste, or *sukumo*), preparation recipes, maintenance procedures, and fermentation phases (Aino et al., 2018; Okamoto et al., 2017). Slow-growing indigo-reducing bacteria are functional bacterial communities that reduce indigo, yet the reduction mechanism of most remains unknown. It may involve the removal of electrons as a metabolic byproduct that passes to indigo particles (Aino et al., 2018). Microbial extracellular electron transfer is the essence of microbial extracellular respiration and part of the anaerobic metabolism of microorganisms. Extracellular respiration refers to the process by which microorganisms completely oxidize organic matter in the cell to release electrons under anaerobic conditions. The generated electrons are transferred to extracellular electron receptors through the intracellular respiration chain and generate energy to maintain their own growth (Lovley et al., 1987; Myers and Nealson, 1988). For example, studies have shown that the electrons of gram-positive bacteria are transferred during direct contact with the pilus or the cell wall (White et al., 2016). Thus, we assume that reducing bacteria will transfer electrons from the inside of the cell to the solid electron acceptor (indigo) outside the cell via the same mechanism (Fig. 6c).

(ii) Low-molecular-weight organic matter, such as flavonoid compounds, can be absorbed and utilized by microorganisms as electron donors (Wu et al., 2016). Thereafter, we assume that the electrons are delivered by analogous mechanisms predicted in the reducing bacteria (Fig. 6d).

(iii) Reducing sugars, such as monosaccharides (glucose and fructose), have been investigated as green reducing agents under alkaline conditions for indigo vat dyeing (Bulut and Elik, 2020; Saikhao et al., 2018; Shin et al., 2016). During the reduction process, the reducing sugar is oxidized, whereas indigo is reduced to leuco-indigo (Boi and Kokol, 2008). For example, the reduction mechanism of glucose in alkaline solutions is associated with a poorly characterized electron-rich intermediate (Ghanem et al., 2005). Hence, we hypothesized that the reducing sugars produced by adding fruits to the traditional indigo dyeing vat may serve as an electron-rich intermediate (Fig. 6e).

In addition to the mechanism of electron transfer through direct contact of insoluble electron acceptors (indigo) with indigo-reducing bacteria, another indirect mechanism of electron transfer exists (Bi et al., 2013; Brutinel and Gralnick, 2013). This is a by-product of microorganism metabolism that acts as an electron mediator between microbial cells and indigo molecules. The electron mediator is first reduced by microorganisms, and subsequently diffuses away from the cell. Upon encountering a suitable electron acceptor (indigo), the electron mediator loses electrons, converts them to their oxidized state, and completes the cycle. Endogenous electron mediators, i.e., quinones yet to be identified, may be excreted by microorganisms (Newman and Kolter, 2000); while exogenous electron mediators (such as quinone-based compounds) may originate from additional plants in the traditional indigo vat (Fig. 6 f). The addition of quinoid redox mediators to anaerobic cultures enhances their reduction rate (Rau et al., 2002).

Indigo-reducing enzymes from microorganisms can also be used for indigo reduction. For example, an enzyme from *Bacillus subtilis* has been shown to reduce indigo in the presence of NADH and a redox mediator that carries electrons from the enzyme to the indigo (Božič et al., 2010). *Clostridium isatidis* produces cellulase with a hydrophobic cellulose-binding domain, which helps break hydrogen bonds in cellulose and presumably acts in a similar manner to hydrogen-bonded indigo particles (Campos et al., 2000). Azoreductase from alkaliphilic *Bacillus* sp. AO1 (Suzuki et al., 2018) and a new reduced NAD^+-dependent azoreductase from *Bacillus cereus* (Pricelius et al., 2007) have shown high potential for catalyzing indigo reduction.

4.3. Overdyeing process

According to the dyeing method applied and the binding mechanism to the fiber, natural dyes can be classified into: direct dyes, mordant dyes, and vat dyes. The exact nature of the "fiber-(mordant)-dye" interaction is unknown (Cardon, 2007).

Mordants are metallic salts of minerals (e.g., alum, ferrous sulfate, iron acetate, copper sulfate, copper acetate) or of plant origin (e.g., aluminum or copper hyperaccumulating species) (İşmal and Yıldırım, 2019) (Fig. 6). Metal mordants function in the binding between fiber and dye, thus increasing color fastness; however, they can also influence the color hue (e.g., black gained from brown tannins + iron mordants) (Cardon, 2007). Tannins have a dual nature: they are dyes and can be used with or without metal mordants. However, tannins can also function as mordants for dyes on cellulose fibers (Cardon, 2007) (Fig. 6). Whether tannins can influence the fastness of indigo dyeing on cellulose fibers is unknown and would need to be tested experimentally.

Cardon (2007) mentioned the combination of dyeing with indigo and tannins in a separate overdying process to yield very dark blue and blue-black colors, describing methods from Central and South America (Roquero, 2006). However, in the Mexican method, tannins are used in the indigo vat and various other plant species, which may function as antioxidants (Cardon, 2007; Oleszek et al., 2001; Piacente et al., 2004; Roquero, 2006).

5. Conclusion and implications for future research

Traditional knowledge of SAC dyeing processes for blue and black is important for the 21st century. In particular, environmental concerns regarding harmful chemicals and environmental pollution from industrial indigo vats are based on chemical reduction with sodium dithionite ($Na_2S_2O_4$).

This research focused on the plant species added to traditional SAC dye vats, suggesting eight testable hypotheses to explain why these products are added to the dye vat or are associated with the process of turning indigo colored cloth to black. Generally, the added products in the traditional indigo dye vat operate based on two principles: providing an alkaline environment and reducing indigo through biological fermentation. Moreover, the overdyeing process in a second dye bath with tannins and/or other metallic mordants may improve color fastness. Consequently, adding specific plant products to SAC dye vats guided by traditional knowledge can provide new insights into commercially viable, low-cost, and environmentally friendly indigo dyeing methods. The hypotheses and explanation model provided in this study, based on an analysis of literature review results and ethnobotanical field research, provide the basis for further research to verify if our assumptions are true. Future experimental research is needed to examine the hypothesized influences of the substances added to the vats on fermentation, final color, and quality (e.g., color fastness) of dyeing. Furthermore, from the perspective of the whole dyeing process, pH in the dye vat does not merely offer alkaline conditions, it also influences other components, such as the production of functional microorganisms or enzymatic reactions. Furthermore, reducing bacteria play a crucial role in the reduction process. Exploring new reducing bacteria in the dyeing solution can artificially control the composition of fermenting microorganisms, thereby directionally improving the quality of the plant indigo dyeing solution and increasing dyeing efficiency.

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CRediT authorship contribution statement

Anthony B. Cunningham and Shan Li all contributed to this work in terms of conceptualizing and writing up this study. Anna Hartl contributed to the hypothesis in an earlier state of the draft and revised parts of the manuscript. Yuhua Wang conceived the study and reviewed the manuscript. Shan Li, Yuru Shi, Zuchuan Qiu, and Xiaoyong Ding conducted interviews in villages in Guizhou and Hainan, China (2019) based on interview protocols developed by Anna Hartl, with some input from Anthony Cunningham. Shan Li also collected information for this study during earlier fieldwork (2016, 2017) in Yunnan, China, which was supplemented by fieldwork by Anthony Cunningham in Indonesia, India, and Laos.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

I have shared the data in the supplementary information.

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Appendix A

1) From where do you get the indigo you use for dyeing?
2) Which ingredients do you use for setting up a vat?

Indigo Other	water	lime	ash lye	plants

3) How long does it take until a newly set up vat is ready for dyeing? *(Please note answer here)*
4) Which kind of fiber material do you dye in the vat?

Plant fibers	cotton other	linen	hemp	ramie	nettle	banana	mullberry
Animal fibers	wool	silk	other				
Synthetic fibers							

5) Which of these colors do you prefer most, and would you like to say why?

Light blue (1)	Blue (2)	Blue (3)	Blue (4)	Dark blue (5)	Very dark blue (6)	Black (7)

Please note down reason why:

6) How do you achieve a colour like that?
7) Which ingredients do you use for maintaining a vat?

indigo	water	lime	ash lye	plants
other				

8) How long do you maintain your vats? *(Please note answer here)*

Appendix B

Plant species and their potential function in the dyeing processes.

Family	Species	Plant parts used	Voucher Specimen number	Application	Local use	Ash source	Micro-organisms source	Food for micro-organisms	Electron mediators	Electron donors	Reducing sugars from fruits	Metallic mordant	Tannin mordant	Symbolic ingredients
Acanthaceae	*Peristrophe bivalvis* (L.) Merr.[a]	L, ST		Vat	BGL									√
Amaranthaceae	*Iresine herbstii* Hook.[a]	L, ST		Vat	BGL									√
Anacardiaceae	*Rhus chinensis* Mill.	Galls		Over	AB								√	
Asclepiadaceae	*Calotropis gigantea* (L.) Dry.ex Ait.f.	R												
Asteraceae	*Ageratum conyzoides* (L.) L.[a]	WPL		Vat	FR					√				
Asteraceae	*Artemisia argyi* H.Lév. & Vaniot	L		Vat	AW	√								
Asteraceae	*Carthamus tinctorius* L.[d]	WPL		Vat	FR				√					
Asteraceae	*Elephantopus scaber* L.	WPL												
Asteraceae	*Tithonia diversifolia* (Hemsl.) A. Gray[a]	L, ST		Vat	FR				√					
Betulaceae	*Alnus nepalensis* D.Don	BK	15LS01	Over	AB								√	
Boraginaceae	*Ehretia microphylla* Lam.	BK, ST, L		Vat	FR				?					
Casuarinaceae	*Casuarina junghuhniana* Miq.	BK												
Combretaceae	*Terminalia bellirica* (Gaertn.) Roxb.[h]	FR		Over	AB								√	
Combretaceae	*Terminalia catappa* L.[g]	L, BK		Over	AB								√	
Combretaceae	*Terminalia chebula* Retz.[h]	FR		Over	AB								√	
Commelinaceae	*Commelina bengalensis* L.	WPL	19QZC013	Vat	ICF							√		
Commelinaceae	*Commelina communis* L.	WPL	19QZC019	Vat	ICF							√		
Cucurbitaceae	*Zehneria japonica* (Thunb.) H.Y. Liu		Sujata 14											

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(*continued*)

Family	Species	Plant parts used	Voucher Specimen number	Application	Local use	Ash source	Micro-organisms source	Food for micro-organisms	Electron mediators	Electron donors	Reducing sugars from fruits	Metallic mordant	Tannin mordant	Symbolic ingredients
Dioscoreaceae	*Dioscorea cirrhosa* Lour.[a]	T	18QZC009	Over	AB								√	
Euphorbiaceae	*Bridelia monoica* (Lour.) Merr.[h]	R, BK												
Euphorbiaceae	*Homalanthus novoguineensis* (Warb.) K. Schum.	L		Over	AB								√	
Euphorbiaceae	*Homalanthus populneus* (Geiseler) Pax	BK, L		Over	AB								√	
Euphorbiaceae	*Macaranga tanarius* (L.) Müll.Arg.	BK, L		Over	AB								√	
Fagaceae	*Castanopsis boisii* Hickel & A.Camus	BK												
Fagaceae	*Quercus acutissima* Carruth.	FR												
Fagaceae	*Quercus wutaishanica* Mayr	FR												
Lamiaceae	*Hyptis suaveolens* (L.) Poit.	ST, FL, L	Sujata 17	Over	ICF							√		
Leguminosae	*Acacia leucophloea* (Roxb.) Willd.	BK		Over	AB								?	
Leguminosae	*Acacia rugata* (Lam.) Fawc. & Rendle[g]	BK			AB								?	
Leguminosae	*Albizia chinensis* (Osbeck) Merr.													
Leguminosae	*Albizia julibrissin* Durazz.													
Leguminosae	*Bauhinia variegata* L.[a]	ST		Vat	AW	√								
Leguminosae	*Caesalpinia sappan* L.	WD		Vat	FR				√					
Leguminosae	*Cassia fistula* L.	BK		Over	AB								√	
Leguminosae	*Dalbergia mimosoides* Franch.	BK		Over	AB								?	
Leguminosae	*Dalbergia odorifera* T.C. Chen	WD		Vat	FR				√					
Leguminosae	*Kummerowia striata* (Thunb.) Schindl.[b]	WPL		Vat	FR					√				
Leguminosae	*Peltophorum pterocarpum* (DC.) K.Heyne													
Leguminosae	*Spatholobus suberectus* Dunn[a]	BK		Over	AB								√	
Loganiaceae	*Buddleja officinalis* Maxim.[a]	ST, FL		Vat	FR					√				
Juglandaceae	*Platycarya strobilacea* Siebold & Zucc.[c]	BH, BK		Over	AB								√	
Malvaceae	*Melochia umbellata* (Houtt.) Stapf													
Malvaceae	*Pterospermum diversifolium* Blume	BK		Over	AB								√	

(*continued on next page*)

(*continued*)

Family	Species	Plant parts used	Voucher Specimen number	Application	Local use	Ash source	Micro-organisms source	Food for micro-organisms	Electron mediators	Electron donors	Reducing sugars from fruits	Metallic mordant	Tannin mordant	Symbolic ingredients
Malvaceae	*Pterospermum niveum* Vidal[g]	BK		Over	AB								√	
Malvaceae	*Sterculia foetida* L.	FR		Vat	AW	√								
Melastomataceae	*Melastoma dodecandrum* Lour.	WPL	19QZC014	Vat	FA					√	?			
Melastomataceae	*Melastoma malabathricum* L.	WPL		Over	ICF							√		
Meliaceae	*Xylocarpus granatum* J. Koenig[g]	BK		Over	AB								√	
Moraceae	*Maclura cochinchinensis* (Lour.) Corner[d, f]	RWD												
Musaceae	*Musa acuminata* Colla	FR		Vat	FA						√			
Myrtaceae	*Eugenia cuprea* (O.Berg) Nied.[d]													
Myrtaceae	*Psidium guajava* L.	FR		Vat	FA						√			
Myrtaceae	*Syzygium cumini* (L.) Skeels[d]													
Myricaceae	*Myrica rubra* (Lour.) Siebold & Zucc.[b]	BK		Vat	FR					√				
Myristicaceae	*Knema elegans* Warb.	BK	15LS02	Over										
Phyllanthaceae	*Aporosa frutescens* Blume[d]	BK		Over	ICF							√		
Phyllanthaceae	*Phyllanthus emblica* L.	BK, BH	15LS03	Over	AB								√	
Phyllanthaceae	*Phyllanthus reticulatus* Poir.	L												
Piperaceae	*Piper bavinum* C. DC.[a]	L		Vat	FR		√							
Plumbaginaceae	*Plumbago indica* L.	WPL		Vat	FR				√					
Plumbaginaceae	*Plumbago zeylanica* L.	R		Vat	BGL									√
Poaceae	*Oryza sativa* L.[a]	L,ST		Vat	AW, FW	√		√						
Poaceae	*Zea mays* L.[a]	RA		Vat	FW			√						
Polygonaceae	*Persicaria hydropiper* L.[a]	WPL		Vat	FR					√				
Polygonaceae	*Reynoutria japonica* Houtt.	R, ST	18QZC008	Vat	FR		√		√					
Rhizophoraceae	*Ceriops decandra* (Griff.) W. Theob.	BK		Over	AB								√	
Rhizophoraceae	*Ceriops tagal* (Perr.) C.B. Rob.	BK		Over	AB								√	
Rhizophoraceae	*Rhizophora mucronata* Lam.	BK		Over	AB								√	
Rubiaceae	*Gynochthodes* sp.													
Rubiaceae	*Morinda citrifolia* L.	RBK		Vat	AB, FR				√				√	
Rubiaceae	*Neanotis hirsuta* (L.f.) W.H. Lewis	WPL	19QZC012	Vat	FR, ICF				?			?		
Rubiaceae	*Psychotria viridiflora* Reinw. ex Blume[e]	L		Vat	FR				?					

(*continued on next page*)

(*continued*)

Family	Species	Plant parts used	Voucher Specimen number	Application	Local use	Ash source	Micro-organisms source	Food for micro-organisms	Electron mediators	Electron donors	Reducing sugars from fruits	Metallic mordant	Tannin mordant	Symbolic ingredients
Rubiaceae	*Uncaria elliptica* R.Br. ex G.Don[d]	L		Over	AB								√	
Rutaceae	*Harrisonia brownii* A.Juss.													
Sapindaceae	*Nephelium lappaceum* L.[d]	BK		Over	AB								√	
Sapindaceae	*Schleichera oleosa* (Lour.) Merr.[f]	BK		Over	AB								√	
Solanaceae	*Capsicum annuum* L.[a]	DF		Vat	FR									
Surianaceae	*Suriana maritima* L.	BK												
Symplocaceae	*Symplocos fasciculata* Roxb.[d]	BK		Over	ICF							√		
Verbenaceae	*Vitex trifolia* L.			Vat	AW	√								

[a](Li et al., 2019);
[b](Liu et al., 2012);
[c](Ma et al., 2019);
[d](Jasper and Pirngadie, 1912);
[e](Linggi, 2001);
[f](Hofmann, 1997);
[g](Brooks, 1910);
[h](Phạm, 2000)

Used parts: BK: bark, **FL:** flowers, **FR:** fruits, **L:** leaves, **R:** roots, **ST:** stems, **T:** tuber, **RBK:** root bark, **RA:** rachis, **DF:** dry fruits, **RWD:** root wood, **WD:** wood, **WPL:** whole plant.

Application: Vat: for use in the indigo vat, **Over:** for use in overdyeing of indigo dyed textiles.

Local use: AB: achieve black, **AW:** ash water, **BGL:** bring good luck, **FA:** fermentation accelerator, **FR:** fermentation recipe, **FW:** fermented wine, **ICF:** increase color fastness.

?: the potential effect of this plant is uncertain.

Appendix B. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2022.115706.

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